Trends in PM$_{2.5}$ emissions, concentrations and apportionments in Detroit and Chicago

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HIGHLIGHTS

- Since 2001, PM$_{2.5}$ concentrations have declined and compositions have changed.
- Changes in methodology limit interpretation of emission inventory trends.
- Quantile regression allows for trend assessment at various relevant percentiles.
- Emissions from vehicles, biomass, and metals sources are of growing importance.

ARTICLE INFO

ABSTRACT

PM$_{2.5}$ concentrations throughout much of the U.S. have decreased over the last 15 years, but emissions and concentration trends can vary by location and source type. Such trends should be understood to inform air quality management and policies. This work examines trends in emissions, concentrations and source apportionments in two large Midwest U.S. cities, Detroit, Michigan, and Chicago, Illinois. Annual and seasonal trends were investigated using National Emission Inventory (NEI) data for 2002 to 2011, speciated ambient PM$_{2.5}$ data from 2001 to 2014, apportionments from positive matrix factorization (PMF) receptor modeling, and quantile regression. Over the study period, county-wide data suggest emissions from point sources decreased (Detroit) or held constant (Chicago), while emissions from on-road mobile sources were constant (Detroit) or increased (Chicago), however changes in methodology limit the interpretation of inventory trends. Ambient concentration data also suggest source and apportionment trends, e.g., annual median concentrations of PM$_{2.5}$ in the two cities declined by 3.2 −3.6%/yr (faster than national trends), and sulfate concentrations (due to coal-fired facilities and other point source emissions) declined even faster; in contrast, organic and elemental carbon (tracers of gasoline and diesel vehicle exhaust) declined more slowly or held constant. The PMF models identified nine sources in Detroit and eight in Chicago, the most important being secondary sulfate, secondary nitrate and vehicle emissions. A minor crustal dust source, metals sources, and a biomass source also were present in both cities. These apportionments showed that the median relative contributions from secondary sulfate sources decreased by 4.2−5.5% per year in Detroit and Chicago, while contributions from metals sources, biomass sources, and vehicles increased from 1.3 to 9.2% per year. This first application of quantile regression to trend analyses of speciated PM$_{2.5}$ data reveals that source contributions to PM$_{2.5}$ varied as PM$_{2.5}$ concentrations decreased, and that the fraction of PM$_{2.5}$ due to emissions from vehicles and other local emissions has increased. Each data source has uncertainties, but emissions, monitoring and PMF data provide complementary information that can help to discern trends and identify contributing sources. Study results emphasize the need to target specific sources in policies and regulations aimed at decreasing PM$_{2.5}$ concentrations in urban areas.

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1. Introduction

Historical ambient air quality monitoring data permit a wide range of trend, apportionment, health risk and other analyses. In

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the U.S., the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Hand, 2011) and the Chemical Speciation Network (CSN) (US EPA, 2014b) have collected ambient data since the mid-1980s that can facilitate these analyses. As examples, trend analyses can help evaluate the effectiveness of mitigation and control measures, e.g., low emission zones (Jones et al., 2012), and receptor models can identify and apportion contributions of pollutant sources. Both trend and apportionment studies can help to evaluate dispersion and exposure models (Haupt, 2005). Monitoring data also have been widely used to estimate exposures for epidemiology and risk studies investigating and predicting the health consequences of pollutant exposure (Park et al., 2010). Such applications are especially important in areas with susceptible populations and where concentrations exceed ambient standards, and for those emission sources that are difficult to characterize or that have changed rapidly, e.g., on-road emissions, due to recent shifts in fuels, emission controls, and fleet mix.

This study examines focuses on Detroit, MI and Chicago, IL, two U.S. Midwestern cities that have high concentrations of industry, extensive vehicle traffic, historical exceedances of air quality standards, and large low income and minority populations that are susceptible to pollutants. These cities were selected due to the length of the data record available, and to contrast trends in the two cities (in adjacent states) potentially differentially affected by the 2008 recession. In Detroit, receptor model apportionments starting in 1985 have identified key $PM_{2.5}$ sources, which include secondary sulfate aerosol (SO_4^-, especially in the summer), secondary nitrate (NO_3^-), metal processing, biomass burning, other manufacturing and industrial operations, vehicle-related emissions (including primary and secondary aerosols from tire and brake wear, and entrained dust), and crustal-derived emissions (Wolff et al., 1985; Morishita et al., 2006, 2011; Buzcu-Guven et al., 2007; Williams et al., 2009; Duvall et al., 2012; Gildemeister et al., 2007; Kundu and Stone, 2014; Hammond et al., 2008). In Chicago, identified $PM_{2.5}$ sources include secondary NO_3^-, secondary SO_4^-, steel operations, (seasonal) road salt, and vehicles (Rizzo and Scheff, 2007; Kim and Hopke, 2007). These apportionments, like most elsewhere, are based on relatively short periods and have not examined trends. (Recent studies in the western U.S. have investigated long term $PM_{2.5}$ apportionment trends (Wang and Hopke, 2013; Hasheminassab et al., 2014)) Updated analyses are needed to account for the many changes in emissions and industrial activity that have occurred over recent decades.

This study's goal is to understand the trends in the sources contributing to $PM_{2.5}$ concentrations in Detroit and Chicago. In each city, we examine emission inventories, ambient pollutant concentrations, and derive source apportionments using receptor models. Quantile regression is used to analyze trends in concentrations and receptor model apportionments, a novel application of this work. Results are compared to earlier studies, and methodological issues are discussed. The study concludes with a discussion of the changing apportionments of $PM_{2.5}$ levels in the two cities and several recommendations.

2. Methods

2.1. Monitoring site description

Monitoring sites in the two cities were chosen based on the $PM_{2.5}$ components measured, the duration and completeness of the monitoring record, and the diversity of nearby sources. The selected sites have speciation records that extend to the early to mid-2000s, and both are part of the Speciation Trends Network (STN), a subset of CSN monitoring sites at which measurements are taken every 3 days (US Environmental Protection Agency, 2011). Fig. 1 shows the

location of these sites and nearby major point sources of $PM_{2.5}$.

The Allen Park ("Detroit") site in south Detroit (AQS ID: 26-163-0001; lat/long: 42.228611/-83.20833) is a non-source and population-oriented monitoring site that has been used to detect impacts from mobile sources (Zhang and Batterman, 2010). It has recorded the highest PM_{10} levels in the area (Simon et al., 2005). The site is located within 200 m of a major interstate highway (I-75). The immediate vicinity is grassy and wooded; a few covered storage tanks are within 100 m; some light industry, trucking firms, suburban areas, etc., are within 1 km; and heavy industry, including refineries, steel production, coke and coal-fired electricity generation are within 15 km. The speciation record began in 2001. Detroit comprises much of Wayne County, which has a population of 1,820,584 (2010) and an area of 1585 km^2 (US Department of Commerce, 2015).

The Com Edison ("Chicago") site is located in an urban neighborhood in south Chicago, IL (AQS ID: 17-031-0063; lat/long: 41.7514/-87.713488) on the grounds of a small facility of the local electrical utility. Nearby emissions sources include rail lines 1 km to the north, and two 6-lane arterials (Routes 50 and 12) located 2 km to the west and south, respectively. Chicago Midway International Airport is 5 km to the northwest. Heavy industry in Calumet and South Chicago, within 20 km, include coal-fired electricity generation, steel mills, and wet corn milling (which emits PM, SO_2 and volatile organic compounds). The speciation record began in 2001, however, instruments were changed in 2005, and so only data after 2005 are considered. Chicago is located within Cook County, which has a population of 5,194,675 (2010) and area of 2448 km^2 (State & County QuickFacts, 2015).

2.2. Emissions inventory of local emission sources

Data from the 2002, 2005, 2008 and 2011 National Emission Inventories (NEIs) (US EPA, 2014c) for Wayne and Cook Counties, which include the cities of Detroit and Chicago, respectively, were extracted to inform apportionments and to help identify emission trends. (The NEIs are revised every three years.) This analysis considers primary $PM_{2.5}$ (i.e., the sum of filterable and condensable $PM_{2.5}$) emissions from point, non-point, on-road mobile, and off-road mobile sources. On-road sources, which include exhaust, brake, and tire wear emissions from light and heavy duty diesel and gasoline vehicles, were separated in the analyses. The NEI technical support documents were consulted to explain methodological changes between NEIs (US EPA, 2014c).

2.3. Ambient data screening and treatment

The pollutants monitored, as well as monitoring techniques and procedures, have changed over the years, and thus some data screening and treatment are required prior to trend analyses. Both sites measured $PM_{2.5}$ using both federal reference methods (FRMs) and non-FRMs. The CSN has measured $PM_{2.5}$ using MetOne SASS and URG samplers (non-FRMs), which collect $PM_{2.5}$ on Teflon filters that are analyzed gravimetrically. Elements are measured by X-ray fluorescence on Teflon filters, ions by ion chromatography on nylon filters, and elemental (EC) and organic carbon (OC) by thermal optical transmittance (TOT) on quartz filters. Most pollutants are measured every third day (MDEQ, 2015; Illinois Environmental Protection Agency (IEPA), 2013a). In 2007, to reconcile differences in OC measurements between CSN and IMPROVE samplers (positive artifacts resulted from the absorption of organic vapors to PM (Dillner et al., 2012)), URG 3000N samplers were placed at CSN sites to measure EC and OC. The higher flow and face velocity of the URG 3000N decreases VOC adsorption and increases OC volatilization, thus lowering OC concentrations (Kotchenruther, 2011). Along with
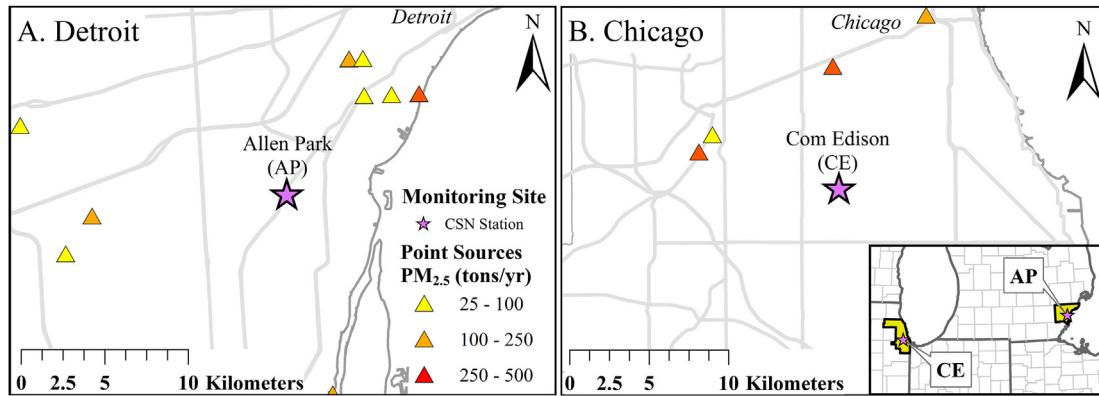
Fig. 1. Maps showing Allen Park, Detroit (A) and Com Edison, Chicago (B) monitoring sites and nearby point sources emitting more than 25 tons of PM$_{2.5}$ in 2011.

the instrument switch, the preferred analysis method also changed from TOT to thermal optical reflectance (TOR), allowing more direct comparisons between CSN measurements of EC and OC to those in the IMPROVE network (which historically used TOR). To assess long-term trends, EC and OC measured using TOT were used in the present work.

Adjustments used prior to trend analyses included blank correction, censoring of values below detection limits, and artifact correction. CSN speciation data are not blank corrected, and for most CSN species, the median trip and field blank concentration is zero (Solomon et al., 2014). (Solomon et al. (Solomon et al., 2014) noted that CSN trip and field blanks can be aggregated.) Each measurement was corrected by the median of blanks taken within ±1 month, as used elsewhere (Dillner et al., 2012; Dutton et al., 2010; Kotchenruther, 2009). Any negative blanks were replaced by the median blank for the entire record. Corrected measurements that fell below method detection limits (DLs) or that became negative were replaced with $^{1}/_{2}$ DL and its measurement uncertainty was replaced with the maximum of the reported uncertainty and $^{5}/_{6}$ DL (Buzcu-Guven et al., 2007). Brown et al. (Brown et al., 2015) gives guidance and reasoning for not censoring those values.

The EC/OC instruments and analytical techniques changed midway through the study period. To address the positive sampling artifact in OC measurements using TOT and the MetOne samplers (Chow et al., 2010), a 2012 EPA memo (Dillner et al., 2012) suggested using monthly median passive network blanks. However, Solomon et al. (Solomon et al., 2014) noted that passive field blanks may miss artifacts arising during active sampling. Fortunately, both Detroit and Chicago sites include one year of collocated MetOne SASS and URG 3000N measurements. These collocated data were regressed as $OC_{MET} = k\ OC_{URG} + artifact$, where k is an estimated regression coefficient used to correct OC MetOne measurements prior to the phase-in of URG samplers (April 2009 in both cities). At Detroit, the regression used the period from 4/1/2009 to 3/30/2010 and gave an OC artifact of 0.126 μg/m^3 and R^2 = 0.77; for EC, R^2 = 0.59. At Chicago, the regression used the period from 5/1/2009 to 4/29/2010 and the estimated OC artifact was 0.303 μg/m^3 and R^2 = 0.85; for EC, R^2 = 0.69. (The Supplemental information provides additional information, including the outliers removed in this analysis.) The estimated OC artifacts are similar to those reported earlier (Dillner et al., 2012; Chow et al., 2010). Future EPA guidance may indicate other methods to harmonize EC and OC data measured using the TOT and TOR methods.

2.4. Quantifying trends

Trends in species concentrations from 2001 to 2014 at Detroit and from 2006 to 2014 at Chicago were evaluated initially using the non-parametric Kruskal-Wallis (KW) and Mann-Whitney (MW) tests, and subsequently using quantile regression (QR). (These analyses used the quantreg (Koenker, 2012) and other packages in R.) Trends in the 'major' PM$_{2.5}$ constituents, defined as species constituting an average of at least 1% by mass of PM$_{2.5}$ (including OC, EC, S, NO$_3^-$, NH$_4^+$, and SO$_4^-$) are of primary interest. Trends in PMF factor mass concentrations and percent contributions were evaluated by QR, as described below.

Initially, the study period was broken into year-blocks (2001—2002, 2002—2005, 2006—2009, 2010—2013, 2013—2015) and seasons (Winter = Dec, Jan, Feb; Spring = Mar, Apr, May; Summer = Jun, Jul, Aug; Autumn = Sept, Oct, Nov). Winter trends were analyzed using data from consecutive months (e.g., winter 2002 data included measurements or apportionments from December 2001 through February 2002). As an initial screen, KW (for 3 or more groups) and MW (for 2 groups) tests attaining a p-value of 0.05 or less were used to identify differences in the distributions between valid groups of measurements, where a valid group was defined as having 10 or more observations with fewer than 50% of observations below DLs. (The direction or magnitude of the differences can be investigated using the Dunn and other tests (Dunn, 1964)).

QR analyses were used to quantify trends of annual median and 90th percentile concentrations, which are exposure measures relevant to chronic and acute health effects, respectively. Trends of peak values may be susceptible to outliers; trends at lower percentiles may be influenced by data censoring. QR also was used to assess trends in relative factor contributions (factor mass divided by total modeled PM$_{2.5}$ mass) to reveal the changing sources of PM$_{2.5}$. Similar to how linear regression coefficients β_i are found by minimizing the sum of squared residuals calculated as $\sum (y_i - (\beta_0 + \beta_1 x_i + ...))^2$, quantile regression coefficients Γ_i are found by minimizing the sum of absolute residuals applied to the function $\rho_\tau, \sum \rho_\tau(\tau, y_i, \xi(x_i, \Gamma))$, where ρ_τ is the "pinball" function at the desired quantile τ, and $\xi(x_i, \Gamma)$ is a linear function of the predictors with Γ_i as coefficients (Koenker and Basset, 1978). The function ρ_τ is equal to $\tau^*(y_i - \xi(x_i, \Gamma))$ if $y_i > \xi(x_i, \Gamma)$ and $(1 - \tau)^*(y_i - \xi(x_i, \Gamma))$ otherwise. Relative (percentage) changes in median and 90th percentile concentrations for calendar years and seasons were quantified by dividing the estimated QR slope by the associated median and 90th percentile concentrations, respectively. Percent per year changes were deemed significant if the QR slope exceeded twice the bootstrapped QR standard error.

2.5. PMF receptor modeling

Ambient data used in the PMF apportionments required additional treatment and quality checks. Missing observations for key

metal species (e.g., Ni, Cr) were replaced with the median, and the associated measurement uncertainty was set to four times the median (Brown et al., 2015). While sometimes the geometric mean is used in place of the median (Hasheminassab et al., 2014), Brown et al. (Brown et al., 2015) recommends investigating scaled residuals when this imputation is performed. For missing uncertainties, formula 5.1 and 5.2 from the User Manual of EPA PMF 5.0 were used for observations above and below DL values, respectively, with an error fraction of 10% (Positive Matrix Factory, 2014). (Only the URG 3000N sampler did not have recorded uncertainties.) CSN data for Detroit and Chicago did not have missing DLs. To increase the reliability and representativeness of PMF results, a minimum of 50 observations per species per year was required. Species selected for PMF were informed by previous studies: Na^+ and K^+ were used preferentially over Na and K given the higher detection frequencies and relevance for air pollution studies (Kim and Hopke, 2005), and $SO_4^=$ rather than S was used as the primary tracer of secondary $SO_4^=$ (both have been used) (Kundu and Stone, 2014; Kim and Hopke, 2005).

To improve reliability and increase fit, PMF apportionments used observations from the cleaned datasets for which 'reconstructed' and observed $PM_{2.5}$ concentrations agreed within ± 4 μg/m^3. Reconstructed mass was calculated using a simplified stoichiometry and the dominant oxidized forms of measured species (shown in square brackets below) (US EPA, 2014)):

$$PM_{2.5,CM} = 1.375 \left[SO_4^=\right] + 1.29 \left[NO_3^-\right] + 3.73 \, [Si] + 1.63 \, [Ca]$$
$$+ 2.42 \, [Fe] + 1.6 \, [OC] + [EC]$$

While agreement might be determined using a multiplicative factor, e.g., within 25%, a concentration band may be more appropriate if errors are primarily additive (rather than multiplicative). The ± 4 μg/m^3 band is reasonably narrow, and fewer than 10% of samples exceeded this criterion. In addition, the holiday periods of 31 December through 2 January and the weekends closest to 4 July were excluded due to the use of fireworks that contain large amounts of potassium nitrate and that can cause deviations from the stoichiometric relationship in eq. (1) (Buzcu-Guven et al., 2007; Rizzo and Scheff, 2007; Brown et al., 2015).

PMF 5.0 calculates a signal-to-noise (S/N) ratio for each species, and S/N < 0.5 is considered 'bad', $0.5 \leq S/N < 1$ 'weak', and $S/N \geq 1$ 'strong'. Weak species are down-weighted in factorization, and bad species are omitted. Additional quality checks included comparisons of elemental and ion concentrations (e.g., S to $SO_4^=$, K to K^+), and comparison of FRM and non-FRM $PM_{2.5}$ concentrations. After treatment, the final Detroit dataset had 1422 observations spanning 14 years (2001–2014), and the Chicago dataset had 763 observations spanning 9 years (2006–2014).

Sources were apportioned using Positive Matrix Factorization (US EPA PMF5.0) (Positive Matrix Factory, 2014) with $PM_{2.5}$ as the 'total' variable (with a designation as 'weak'). Introduced in 1995 (Paatero and Tapper, 1994), PMF apportions sources using the following equation: $X = ZC + E$, where $X = nxm$ matrix of observed concentrations (μg/m^3) values; n = number of observations; m = number of chemical species), $Z = n \, x \, p$ matrix of apparent source strengths; p = user-assigned number of factors or source categories; $C = pxm$ matrix of derived source compositions; and $E = nxm$ matrix of random errors (Paatero and Tapper, 1994; Antilla et al., 1995). Error terms are scaled by estimates of observation-level uncertainty, and Z and C are constrained to be non-negative. X is solved to minimize the sum of squares of weighted residuals, $Q = \sum_{i=1}^{n}\sum_{j=1}^{m} E_{ij}^2 / \sigma_{ij}^2$, where σ_{ij} = standard deviation of the random errors, which are assumed known. From the solution, the strength and composition of each of p factors can be viewed. Some

PMF factor mass values are allowed to go slightly negative (Positive Matrix Factory, 2014), so to maintain the property of each row-normalized PMF sample summing to 1 (critical for assessing factor fractional contribution trends); these slightly negative values were not censored in trend analyses. (At both cities, fewer than 15% of final factors were negative.)

A range of "additional modeling uncertainties" (e.g., 0, 5, and 10%) were tested using features in PMF5.0. Selection of the number of factors and uncertainty additions depends on prior knowledge of potential sources, source-receptor relationships, and the stability of results (Antilla et al., 1995). The initial models included 6 to 10 factors. A framework for choosing the 'final' model used a series of checks examining the distribution of species within each factor: separation of K^+ and OC; the vehicle factor should contain large fractions of total OC and EC mass and minimal amounts of other species; a crustal factor (Si, Ti, Ca, Al) should emerge; and metals (Ni, Cr, Fe, Mn) should be grouped together. Finally, using PMF 5.0's bootstrapping capability to estimate uncertainties, realized factors should be robust and handle additional model uncertainty.

3. Results

3.1. Emission inventory trends

Table 1 summarizes $PM_{2.5}$ emissions reported in the 2002 through 2011 NEI data. The NEI source categories, data and emission factors have shifted over the years, resulting in large changes and some difficulty in evaluating trends. The methodological changes can greatly affect results and limit its usefulness for trend analyses, at least for certain source types. For example, fugitive emissions of $PM_{2.5}$ from paved roads, unpaved roads, and construction sources are calculated by applying a factor to modeled PM_{10} emissions (Pace, 2005), which itself is estimated using emission factors, activity estimates, and other data. These factors have been updated several times since 2002 (US EPA, 2014c; US EPA, 2014a), which partially explains the large changes in construction dust emissions. Uncertainties in the multiplicative factor used to generate $PM_{2.5}$ emissions from PM_{10} emissions have been discussed at length by Pace (Pace, 2005). As a second example, on-road emissions were calculated over the study period using several models, i.e., the National Mobile Inventory Model (NMIM) running MOBILE6 in 2002, 2005, and version 1 of the 2008 NEI; and then the Motor Vehicle Emission Simulator (MOVES) in versions 2 and 3 of NEI 2008 and 2011. (For non-road mobile emissions, NMIM is still used (US EPA, 2014c).) For mobile sources, important uncertainties include the availability and accuracy of the data providing on-road and off-road gasoline and diesel fuel consumption, the age and composition of the fleet, and the emission factors (Dallmann and Harley, 2010). In addition, not all data in the inventory is updated each period, e.g., the 2005 non-point emissions mostly used the 2002 NEI estimates (US EPA, 2005). Uncertainties in the NEI data also limit many comparisons. With these caveats, we discuss emission trends in the two cities.

Over the study period in Wayne County (encompassing Detroit), NEI point source emissions decreased from 5364 to 1610 tons/year, non-road mobile sources decreased from 855 to 493 tons/year, and on-road mobile emissions (mostly diesel exhaust) fluctuated from a low of 916 (2005) to a high of 2110 tons/year (2008). On-road mobile $PM_{2.5}$ exhaust emissions increased slightly over the study period: both gasoline and diesel vehicle exhaust emissions dropped in 2005, but then nearly doubled in 2008. Non-point source emissions (excluding mobile sources) also fluctuated, from 1682 tons/year (2002) to 5782 tons/year (2008), and of the sources in this category, construction dust had the greatest changes, increasing 25-fold from 2005 to 2008 (to 350 tons/year), then

decreasing by the same amount in 2011. Other non-point sources, primarily residential wood combustion, commercial cooking and various industrial processes (550, 450 and 586 tons/year in 2011, respectively), collectively represent the largest fraction of $PM_{2.5}$ emissions in the inventory (45% in 2011). These non-point emissions had large changes from 2005 to 2011, e.g., residential wood combustion increased from 69 (2005) to 1649 tons/year (2008). The large (over 3-fold) increase in non-point source emissions between 2005 and 2008 was due mostly to updated estimates of fugitive dust.

Emission trends for Cook County (including Chicago) reflect those in Wayne County with several exceptions. First, point source emissions stayed fairly constant (2390 to 2510 tons/year, excluding much higher emissions in 2005), compared to the large decreases in Wayne County. Second, Cook County had very high emissions of construction dust (up to 6351 tons/year, 31% of total $PM_{2.5}$ in 2011), possibly resulting from construction activities (including a number of high-rise buildings), high wind speeds that increase entrainment (Schmeling, 2003), and changes in the calculation methods (noted above). As in Wayne County, non-point sources exhibited an over 3-fold increase from 2005 to 2008, and on-road mobile gasoline and diesel exhaust emissions dropped in 2005 but then approximately doubled in 2008. Non-road mobile sources steadily decreased to 7% of total $PM_{2.5}$ emissions in 2011.

Comparing the two cities, mobile on-road $PM_{2.5}$ emissions were constant in Detroit (1126 to 1188 tons/year) and increased in Chicago (1782 to 2163 tons/year in Cook County) over the study period. On-road mobile sources represented 10—17% of total $PM_{2.5}$ emissions (depending on year and city). On an area basis, however, mobile emissions in the two cities were similar, i.e., 0.75 and 0.88 tons/year/km^2 in Wayne and Cook Counties, respectively (2011 data). On-road emissions were dominated by heavy-duty diesel vehicle exhaust (comprising 61% of emissions in this category in 2011), followed by light-duty gasoline vehicle exhaust (28%). Non-road mobile source emission rates were also 1.5 to 2 times higher in Cook County, but similar on an areal basis, and the largest source in both cities was exhaust from off-road diesel construction vehicles. Diesel railroad emissions in Wayne Country were small (29 tons/year in 2002—5, dropping to 0.5 tons/year in 2008—11), compared to initially much higher levels in Cook County (555 tons/year in 2002—5, but these emissions also plummeted to only 2.8 tons/year in 2008—11). These differences may reflect the higher rail activity in Chicago, effects of controls imposed by the 2004 rules for heavy duty diesel vehicles (US EPA, 2004), the 2008 rules for locomotives (US Environmental Protection Agency, 2014), and other fleet and emission factor changes.

The large uncertainties in nonpoint emissions, the changing methodology in mobile source emissions, and potentially other issues in the emissions inventory data can severely limit trend analyses of the emissions data. Still, several broad trends are apparent. In 2011, on-road emissions exceeded non-road mobile emissions in both cities, and the total mobile emissions matched (Detroit) or exceeded (Chicago) point source emissions. These data suggest several factors that may have affected emissions. In Detroit, the steady decline in point source emissions can be attributed to cleaner fuels (natural gas has replaced considerable coal), updated emission controls on some facilities, and reduced activity in automobile manufacturing and other industries, witnessed by the shuttering of businesses and the continued exodus of a large fraction of the population (State & County QuickFacts, 2015), particularly during the 2008—9 recession. In Chicago, industrial and commercial activity is more diversified (e.g., manufacturing, publishing, finance/insurance, food processing, transport/distribution), the population has been more stable, and the recession's impact on local emitters was likely smaller (e.g., the largest local $PM_{2.5}$ source, a wet corn mill at Corn Products International, likely responds less to economic fluctuations than vehicle manufacturing). Estimates of traffic activity in both cities showed only small changes, e.g., vehicle miles traveled (VMT) in Detroit decreased by 2% since 2004 (Michigan Department of Transportation (MDOT), 2013b), and Chicago did not have a consistent trend (Rodriguez, 2011). In both cities, the switch to low-sulfur diesel fuel in combination with introduction of particle traps have reduced diesel exhaust emissions, although this may be offset by the growth in the number of trucks, based on state-level data.

For comparison, we investigated recent regional or national apportionment studies that analyzed NEI data. Using NEI data from 2002 through 2011 and predefined source profiles in a chemical mass balance (CMB) model in the southeast US, point source emissions showed large decreases, while mobile source emissions showed comparable or smaller decreases (Blanchard et al., 2013). The largest sources identified by a Bayesian source apportionment model, which used CSN data in Boston and Phoenix from 2000 onwards, NEI 2002 data, and profiles from the SPECIATE database, were coal and oil combustion, vegetative burning, road dust, and vehicles (Hackstadt and Peng, 2014). A hybrid receptor-chemical transport model (CTM) using projected NEI 2002 data in six major US cities indicated that coal combustion and on-road gasoline

Table 1
Summary of emissions inventory data in Detroit and Chicago. Expressed as short tons/yr of $PM_{2.5}$ primary (filterable + condensable) and % of total $PM_{2.5}$. Derived from NEI.

Year	Point sources	On-road Mobile			Non-road Mobile		Non-point sources			Total
		Diesel Ex.[a]	Gas Ex.[b]	Other	Diesel Ex.[a]	Other	Construction[c]	Paved road[d]	Other[e]	
Detroit										
2002	5364 (59%)	724 (8%)	245 (3%)	156 (2%)	567 (6%)	288 (3%)	14 (0%)	136 (2%)	1532 (17%)	9026
2005	4402 (57%)	589 (8%)	164 (2%)	163 (2%)	547 (7%)	155 (2%)	14 (0%)	136 (2%)	1550 (20%)	7720
2008	2345 (22%)	1380 (13%)	521 (5%)	209 (2%)	378 (4%)	140 (1%)	350 (3%)	627 (6%)	4805 (45%)	10,754
2011	1610 (23%)	725 (10%)	335 (5%)	128 (2%)	350 (5%)	143 (2%)	18 (0%)	573 (8%)	3194 (45%)	7076
Chicago										
2002	2394 (21%)	1191 (10%)	305 (3%)	285 (3%)	2277 (20%)	503 (4%)	72 (1%)	176 (2%)	4154 (37%)	11,357
2005	3591 (30%)	965 (8%)	254 (2%)	299 (2%)	2125 (17%)	497 (4%)	72 (1%)	176 (1%)	4169 (34%)	12,147
2008	2510 (11%)	2025 (9%)	795 (4%)	383 (2%)	1085 (5%)	494 (2%)	5743 (26%)	917 (4%)	8496 (38%)	22,448
2011	2451 (12%)	1297 (6%)	565 (3%)	301 (1%)	1006 (5%)	492 (2%)	6351 (31%)	1181 (6%)	6595 (33%)	20,239

[a] Diesel Ex. = diesel exhaust.
[b] Gas Ex. = gasoline exhaust.
[c] Construction = construction dust for the county.
[d] Paved Road = paved road dust for the county.
[e] In NEI 2002 and 2005, mobile emissions are not included in non-point emissions, while in NEI 2008 and 2011, mobile emissions are included in non-point emissions. In this table, "Other" non-point sources do not include mobile emissions.

emissions were the largest sources of primary and secondary PM$_{2.5}$ (Hu et al., 2014). Using fuel-based estimates from on- and non-road mobile sources in California, a range of vehicle types showed decreases in emissions and the growing contribution of non-road mobile sources relative to on-road sources (McDonald et al., 2015). Although these earlier studies have some similarities to the present study, they neither compared NEI data with CSN data and PMF results over the same period nor investigated long-term trends from mobile sources in the Midwest, the focus of this work. Lastly, we note that year-to-year emissions of other criteria pollutants (SO$_2$, CO, NO$_x$) tend to be more stable than PM$_{2.5}$, probably because the underlying data (e.g., emission and activity factors) are more robust and less subject to large methodological changes.

3.2. Concentration trends

Table 2 summarizes annual and seasonal ambient concentrations in the two cities, including test results showing differences between year-blocks. (The supplemental information contains expanded versions of this table.) Several PM$_{2.5}$ constituents show considerable seasonal variation, e.g., NO$_3^-$ levels tended to be highest in winter and fall, and S and SO$_4^=$ were highest in summer, thus, seasonal analyses are needed to understand trends.

In Detroit, concentrations of PM$_{2.5}$, NH$_4$, NO$_3^-$, SO$_4^=$ and many other species changed significantly between year-blocks ($p < 0.05$ for KW and MW tests); in contrast, changes in EC and usually OC concentrations were not statistically significant. Comparing the 2006–2009 and 2013–2015 periods, for example, median SO$_4^=$ concentrations fell 33% (from 2.36 to 1.57 μg/m^3), while median EC (URG sampler) levels were unchanged (0.32 and 0.33 μg/m^3). Most species decreased less rapidly than SO$_4^=$, e.g., median PM$_{2.5}$ concentrations decreased only slightly (10.9–10.6 μg/m^3), although 90th percentile PM$_{2.5}$ levels fell from 23.4 to 17.5 μg/m^3. Seasonal statistics are similar. In Chicago, concentrations were more stable, e.g., only NH$^+$ and SO$_4^=$ changed annually and in each season, and PM$_{2.5}$, NO$_3^-$ and S concentrations varied annually and in winter and fall seasons. Concentrations tended to decrease from 2006 to 2009 to 2010–2013, however, levels after 2013 sometimes increased. Again, EC and OC showed smaller and fewer significant differences compared to the other species. The instrument switch in spring 2010 likely dampened EC and OC trends.

Across the two cities, QR results showed that 50th and 90th percentile concentrations of PM$_{2.5}$ and many of the major species significantly decreased over the study period (Figs. 2 and 3). In Detroit, median concentrations of PM$_{2.5}$ fell by 3.6%/yr, and seasonal decreases from 2.7 (winter) to 4.9 (spring) %/yr. At the 90th percentile, PM$_{2.5}$ concentrations declined slightly faster with annual levels falling by 4.9%/yr and seasonal decreases from 3.5 (winter) to 5.6 (summer) %/yr. Annual and seasonal trends of NH$_4^+$ and NO$_3^-$ (at both percentiles) were nearly identical, e.g., median levels decreased by 7.0 and 5.5%/yr overall, and declines were fastest in spring (8.6 and 8.2%/yr) and slowest in winter (5.4 and 3.6%/yr); 90th percentile concentrations decreased fastest in summer (9.5 and 8.8%/yr) and slowest in winter (3.4 and 2.1%/yr). Unsurprisingly, SO$_4^=$ and S trends were nearly identical, e.g., median concentrations decreased by 5.8 and 4.9%/yr overall, and changes were the smallest in winter (4.0 and 2.9%/yr) and similar in other seasons (4.8–5.9%/yr); 90th percentile levels fell fastest in fall (9.2 and 8.9%/yr) and slowest in winter (3.6 and 2.8%/yr). QR results for the two types of EC measurements differed, e.g., EC$_{MET}$ levels did not change at annual and seasonal levels other than a 2.7%/yr decrease seen in the median summer levels, while EC$_{URG}$ decreased by 5.0 and 5.8%/yr at median and 90th percentile levels, respectively, largely due to decreases in fall and spring, respectively.

OC$_{MET}$ and OC$_{URG}$ also showed differences, e.g., median OC$_{MET}$ levels decreased by 6.5%/yr on an annual level and from 4.6 (summer) to 8.5 (fall) %/yr on a seasonal basis; OC$_{URG}$ did not show significant changes in any season or percentile. Overall, the seasonal patterns of PM$_{2.5}$, NH$_4^+$ and NO$_3^-$ were similar. The shorter time series of EC and OC available for each instrument may have obscured trends. In the following PMF application, a complete record of adjusted EC and OC concentrations is used to derive long-term trends.

Chicago showed fewer trends that were statistically significant, as well as less consistency across related species (Fig. 3). Median and 90th percentile levels of PM$_{2.5}$ dropped by 3.2 and 4.1%/yr, respectively, and summer and fall changes at the 90th percentile were significant (7.6 and 5.3%/yr). Decreases in median levels of NH$_4^+$ (8.6%/yr) were slightly larger than changes in Detroit, and decreases in summer and fall were particularly rapid (13.5 and 14.2%/yr). For NO$_3^-$, statistically significant decreases were only seen in fall (median and 90th percentile) and winter (90th percentile), and NO$_3^-$ and NH$_4^+$ changes were not correlated, unlike in Detroit. SO$_4^=$ and S trends in Chicago also differed from those in Detroit: the largest decreases occur in summer (10.0 and 7.3%/yr for medians), and the smallest in both winter and spring. (Detroit's largest changes for SO$_4^=$ and S were in fall and the smallest in winter.) EC and OC trends in Chicago were less pronounced and few attained statistical significance, however, there were some similarities in EC trends with patterns observed in Detroit. Median levels of EC$_{MET}$ decreased greatly in summer (15.2%/yr); and both median and 90th percentile levels of EC$_{URG}$ fell significantly (3.6 and 5.1%/yr). Seasonal concentrations of OC$_{MET}$ fluctuated (both increased and decreased) across the study period, but changes were not statistically significant. Since only three years of data (2006 to early 2010) were available for the Chicago EC$_{MET}$ and OC$_{MET}$ measurements, trends for these variables are not reliable. Median and 90th percentile concentrations of OC$_{URG}$ decreased (1.9 and 3.9%/yr). Overall, PM$_{2.5}$ concentrations in Chicago and Detroit decreased at similar rates, but few of the major constituents in Chicago showed seasonal trends that were significant or consistent with Detroit's.

Many of the major species (e.g., NH$_4^+$, NO$_3^-$, SO$_4^=$ and S) had greater changes across the study period in summer and fall when concentrations were higher, as compared to winter when concentrations were often lower. In Detroit, trends in annual median NO$_3^-$ and NH$_4^+$ concentrations were driven more by changes in spring and less by changes in winter; peak concentrations were driven more by changes in summer peaks and less (again) by changes in winter peaks. Similarly, changes in annual median SO$_4^=$ and S concentrations were driven less by changes in winter; changes in peak SO$_4^=$ and S were also highest in summer and fall. Trends in median and peak PM$_{2.5}$ concentrations most resembled patterns for the nitrogen components, which suggests that in Detroit changes in NO$_3^-$ exerted a greater influence on PM$_{2.5}$ levels than SO$_4^=$. This result is unexpected since NO$_3^-$ and NH$_4^+$ comprise a smaller PM$_{2.5}$ fraction than OC and SO$_4^=$, however, this analysis does not consider a mass balance (e.g., reconstructed mass) or account for correlated species and source contributions (as described in the PMF modeling following). Trends in Chicago have some similarities, but also notable differences: trends in peak PM$_{2.5}$ concentrations resembled patterns for SO$_4^=$ rather than NO$_3^-$; reductions in SO$_4^=$ and S in summer and fall were the highest among seasons, and only peak PM$_{2.5}$ trends in summer and fall were statistically significant. This pattern also conforms to the KW and MW test results, and suggests that PM$_{2.5}$ levels in Chicago aligned more with changes in SO$_4^=$ than NO$_3^-$.

Both regional and local sources influence concentration trends. Secondary regional pollutants are important constituents of PM$_{2.5}$ in the Midwest, and much of the SO$_4^=$ in the region results from long range transport from large coal-fired boilers and power plants.

Table 2
Median and 90th percentile concentrations by year-block and statistical differences between year-block concentrations. Differences based on Kruskal-Wallis (comparing 3 + groups) or Mann-Whitney (comparing 2 groups) tests, and α = 0.05, with at least 10 valid observations per group.

Species		All						Winter						Spring						Summer						Fall					
		2001	2002	2006	2010	2013		2001	2002	2006	2010	2013		2001	2002	2006	2010	2013		2001	2002	2006	2010	2013		2001	2002	2006	2010	2013	
		2002	2005	2009	2013	2015		2002	2005	2009	2013	2015		2002	2005	2009	2013	2015		2002	2005	2009	2013	2015		2002	2005	2009	2013	2015	
Detroit																															
PM$_{2.5}$	50th	13.0	12.7	10.9	8.9	10.6	†	20.8	12.9	13.2	9.8	13.1	†	14.2	11.9	8.5	7.8	8.3	†	13.2	14.7	11.2	11.2	10.9	†	10.5	11.1	9.8	7.8	11.4	†
	90th	32.4	26.8	23.4	18.2	17.5		38.0	26.8	24.7	19.9	21.6		27.0	24.2	21.1	15.7	13.6		35.4	30.2	22.7	19.3	15.5		25.1	28.2	23.8	16.8	17.4	
NH$_4^+$	50th	1.42	1.66	1.29	0.76	0.94	†	2.22	1.78	2.05	1.15	1.05	†	1.56	1.76	1.13	0.76	0.98	†	1.43	1.53	1.08	0.67	0.65	†	0.74	1.36	1.09	0.54	0.49	†
	90th	5.16	4.35	3.70	2.31	2.57		5.84	4.14	3.93	3.12	3.02		3.94	4.33	3.49	1.88	2.19		5.98	4.26	3.06	1.79	1.78		3.81	4.79	3.80	1.77	1.86	
NO$_3^-$	50th	1.59	2.01	1.44	1.07	1.69	†	4.40	3.57	3.65	2.59	3.08	†	2.29	2.71	1.49	1.09	1.98	†	1.31	0.91	0.65	0.55	0.59	†	1.15	1.86	1.27	0.97	0.95	†
	90th	8.17	6.67	5.98	4.12	6.35		13.7	9.32	8.08	6.69	7.17		8.40	6.86	5.65	3.32	4.36		3.97	3.19	1.96	1.48	1.53		4.48	5.75	4.49	3.20	3.73	
SO$_4^-$	50th	3.02	2.73	2.36	1.56	1.57	†	3.09	2.16	2.55	1.47	1.52	†	2.68	2.94	2.19	1.64	1.53	†	3.33	4.13	2.84	2.22	2.40	†	2.28	2.43	1.93	1.28	1.42	†
	90th	9.82	8.27	5.59	4.02	3.13		8.10	4.44	4.06	3.28	3.07		7.49	6.22	5.24	3.27	3.02		15.6	11.0	7.46	5.52	4.36		7.94	9.87	5.89	3.37	3.02	
S	50th	0.99	0.91	0.78	0.56	0.56	†	1.04	0.71	0.81	0.50	0.56	†	0.85	0.95	0.73	0.56	0.54	†	1.03	1.39	0.96	0.85	0.83	†	0.85	0.78	0.68	0.45	0.49	†
	90th	3.20	2.64	1.83	1.42	1.16		2.49	1.52	1.34	1.19	1.06		2.27	2.11	1.68	1.12	1.14		4.83	3.67	2.47	2.01	1.61		2.69	3.25	2.05	1.24	1.16	
EC$_{MetOne}$[a]	50th	0.59	0.66	0.65	0.63	—	°	0.54	0.58	0.56	0.62	—	°	0.43	0.54	0.48	0.91	—	†	0.76	0.80	0.72	—	—	°	0.67	0.77	0.79	0.40	—	°
	90th	1.05	1.25	1.26	1.49	—		1.02	1.02	0.90	1.43	—		0.82	0.96	0.99	1.70	—		1.06	1.37	1.24	—	—		1.03	1.46	1.59	0.40	—	
EC$_{URG3k}$[b]	50th	—	—	0.32	0.38	0.33	°	—	—	—	0.30	0.32	°	—	—	0.25	0.33	0.29	°	—	—	0.37	0.45	0.43	°	—	—	0.42	0.45	0.38	°
	90th	—	—	0.84	0.73	0.67		—	—	—	0.55	0.58		—	—	0.56	0.63	0.51		—	—	0.68	0.81	0.73		—	—	0.94	0.85	0.94	
OC$_{MetOne}$[a]	50th	2.87	2.81	2.11	1.19	—	†	3.63	2.48	1.84	1.17	—	†	2.62	2.55	1.82	2.24	—	†	3.69	3.76	3.13	—	—	†	2.63	2.58	1.77	1.17	—	†
	90th	5.93	5.63	4.86	3.18	—		7.63	5.19	4.82	2.82	—		4.76	4.30	3.98	4.61	—		6.13	6.71	5.15	—	—		5.73	4.98	4.77	1.17	—	
OC$_{URG3k}$[b]	50th	—	—	1.76	1.85	1.83	°	—	—	—	1.62	1.73	°	—	—	1.41	1.49	1.62	°	—	—	1.95	2.34	2.23	†	—	—	1.99	1.79	1.87	°
	90th	—	—	3.76	3.42	3.53		—	—	—	3.06	3.48		—	—	2.34	2.89	2.98		—	—	3.21	4.04	3.50		—	—	4.58	3.40	4.52	
Chicago																															
PM$_{2.5}$	50th	—	—	10.9	9.4	9.7	†	—	—	12.7	9.8	10.7	†	—	—	10.2	9.5	8.55	°	—	—	10.7	10.6	9.85	°	—	—	10	7.7	9.45	†
	90th	—	—	22.3	18	19.3		—	—	21.9	19.9	23.3		—	—	21.3	18.2	18.9		—	—	24.4	16.7	16		—	—	21.9	17.2	14.4	
NH$_4^+$	50th	—	—	1.40	0.79	0.95	†	—	—	2.02	1.11	1.36	†	—	—	1.27	0.94	1.04	†	—	—	1.11	0.62	0.57	†	—	—	1.19	0.55	0.66	†
	90th	—	—	3.70	2.39	2.79		—	—	4.15	3.28	3.15		—	—	3.44	2.48	2.86		—	—	3.08	1.59	1.69		—	—	3.53	1.92	1.74	
NO$_3^-$	50th	—	—	1.62	1.14	2.00	†	—	—	4.19	2.75	3.60	†	—	—	1.82	1.58	2.47	°	—	—	0.69	0.60	0.68	°	—	—	1.43	0.81	1.18	†
	90th	—	—	6.46	5.14	7.14		—	—	8.60	8.11	8.47		—	—	5.68	4.15	7.33		—	—	2.35	1.37	3.24		—	—	6.18	3.50	3.94	
SO$_4^-$	50th	—	—	2.12	1.60	1.48	†	—	—	2.38	1.44	1.38	†	—	—	2.02	1.69	1.56	†	—	—	2.51	1.77	1.76	†	—	—	1.92	1.25	1.25	†
	90th	—	—	5.51	3.72	3.30		—	—	3.85	3.42	2.75		—	—	4.56	3.78	3.30		—	—	7.73	4.82	3.73		—	—	5.97	3.22	3.02	
S	50th	—	—	0.72	0.57	0.51	†	—	—	0.80	0.50	0.51	†	—	—	0.67	0.58	0.57	°	—	—	0.86	0.72	0.67	°	—	—	0.66	0.47	0.45	†
	90th	—	—	1.83	1.35	1.16		—	—	1.33	1.12	0.97		—	—	1.55	1.25	1.16		—	—	2.62	1.64	1.37		—	—	1.96	1.19	1.04	
EC$_{MetOne}$[a]	50th	—	—	0.62	0.82	—	°	—	—	0.54	0.71	—	°	—	—	0.61	0.88	—	°	—	—	0.66	—	—		—	—	0.66	—	—	
	90th	—	—	1.25	1.36	—		—	—	0.95	1.15	—		—	—	1.30	1.44	—		—	—	1.40	—	—		—	—	1.16	—	—	
EC$_{URG3k}$[b]	50th	—	—	0.42	0.36	0.34	†	—	—	0.33	0.29	0.33	°	—	—	0.35	0.36	0.31	°	—	—	0.45	0.43	0.46	°	—	—	0.46	0.38	0.36	†
	90th	—	—	0.84	0.76	0.66		—	—	0.61	0.55	0.53		—	—	0.70	0.77	0.61		—	—	0.88	0.83	0.69		—	—	1.02	0.76	0.80	
OC$_{MetOne}$[a]	50th	—	—	2.65	2.21	—	†	—	—	1.94	1.70	—	°	—	—	2.59	2.31	—	°	—	—	3.60	—	—		—	—	2.40	—	—	
	90th	—	—	4.71	4.21	—		—	—	3.74	4.10	—		—	—	4.06	4.40	—		—	—	6.09	—	—		—	—	3.98	—	—	
OC$_{URG3k}$[b]	50th	—	—	2.15	1.93	1.94	†	—	—	2.17	1.69	1.70	†	—	—	1.70	1.82	1.73	°	—	—	2.33	2.40	2.33	°	—	—	2.19	1.87	2.04	°
	90th	—	—	3.89	3.59	3.17		—	—	3.26	2.87	2.98		—	—	3.64	3.44	2.89		—	—	4.02	3.94	3.89		—	—	4.41	3.64	3.23	

† Reject the null hypothesis.
° Do not reject the null hypothesis.
[a] The Met One SASS sampler was used until 3/30/10 at Detroit and 4/29/10 at Chicago.
[b] The URG 3000N sampler was used starting 4/1/09 at Detroit and 5/3/07 at Chicago.
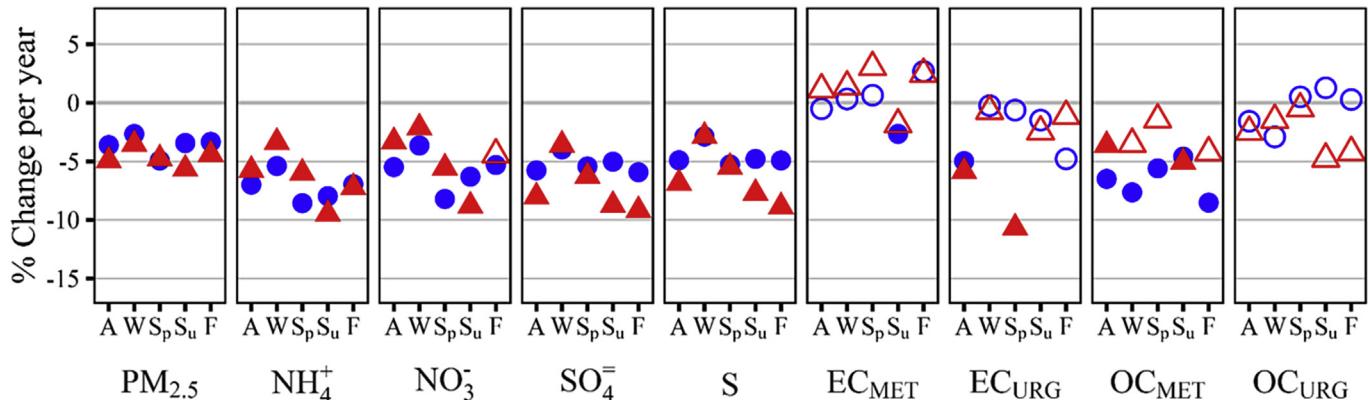
Fig. 2. Annual and seasonal concentration trends in Detroit from 2001 to 2015. Shows annual changes in median concentrations as blue circles (●, o) and in 90th percentile concentrations as red triangles (▲, Δ) for selected major species, expressed as %/yr for all seasons (A), winter (W), spring (Sp), summer (Su) and fall (F). Based on quantile regressions of ambient measurements. Filled symbols (e.g., ●) are statistically significant, i.e., trend exceeded 2-times its bootstrapped standard error. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
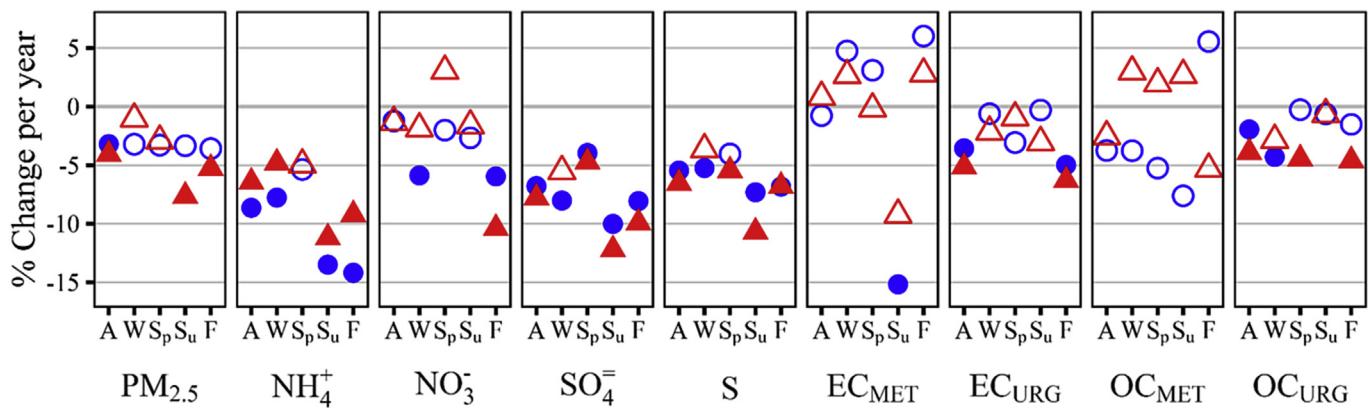
Fig. 3. Annual and seasonal concentration trends in Chicago for median and 90th percentile concentrations from 2006 to 2014. Otherwise as Fig. 2.

Many of these facilities have reduced emissions of precursor SO_2 in recent decades by the addition of scrubbers and fuel switching. In cases, such changes have not occurred for the generally smaller and often older coal-fired facilities located in cities, a result of space constraints, costs and other issues. NO_3^-, another secondary pollutant from precursor NO and NO_2 emissions (largely from mobile sources and power plants), often has the highest levels in winter and spring when O_3 concentrations are low (Parrish et al., 1991). Both $SO_4^=$ and NO_3^- are present in the Midwest atmosphere as ammonium sulfate and ammonium nitrate due to ammonia emissions from fertilizers and animal feed (US EPA, 2008a). OC is derived from primarily vehicle emissions and biomass burning (Kundu and Stone, 2014). The largest contributor to EC is diesel exhaust emissions (Reff et al., 2009). Road dust contributions (i.e., Si, Ti, Ca, Al) are normally low in winter due to lower siltation levels (Fraser et al., 2003). Concentrations of major species in both cities followed expected seasonal trends (Bell et al., 2007), e.g., NH_4^+ and NO_3^- were highest in the winter, $SO_4^=$ was highest in the summer, and EC and OC were higher in summer than winter.

Overall, median $PM_{2.5}$ concentrations in the two cities declined by 4.3–4.5%/yr: comparable rates have been shown in several national and regional assessments. Nationally, a 27% drop in average $PM_{2.5}$ from 2000 to 2010 (2.7%/yr) has been reported US EPA, 2014d; Rao et al., 2012). The Lake Michigan Air Directors Consortium (LADCO) estimate a 0.51 μg/m³ per year decrease in 90th percentile $PM_{2.5}$ concentrations from 1999 to 2007 across the region (Adamski et al., 2009), which (when converted) is in the range of %/yr decreases in the present work. The monitoring data also reveal the changing composition of $PM_{2.5}$: the share is growing for EC and OC, but declining for $SO_4^=$ and NO_3^-. While many sources emit EC and OC, local vehicle emissions are one of the larger contributors (Fraser et al., 2003; Schauer et al., 1996; Subramanian et al., 2006). In contrast, $SO_4^=$ largely arises from local and regional point sources (Wolff et al., 1985). The less pronounced trends at Chicago may reflect the shorter study period, as well as smaller changes in the local and regional sources.

Trends in the ambient monitoring data have some consistencies with the emissions inventory data discussed earlier, particularly for the combustion sources (point and mobile exhaust; Table 1). For example, ambient levels of $SO_4^=$, NO_3^-, and NH_4^+ in Detroit fell by 5–10%/yr over the 2002 and 2011 study period, while point source emissions decreased by roughly 11%/yr. In contrast, ambient levels of EC showed few significant changes, consistent with fluctuating trends of on-road diesel exhaust emissions. In Chicago, $SO_4^=$ and NH_4^+ also decreased significantly from 2006 to 2014, and the emissions inventory showed a concurrent drop in point source emissions. As noted earlier, a number of issues in the emissions inventories limits the comparability of trends.

Concentration trends also can be framed in the context of species abundance (i.e., species concentration/$PM_{2.5}$ concentration on a per-sample basis). However, given issues with EC and OC measurements (key tracers for vehicle emissions), uncertainties in the

stoichiometric balance, and the correlation among both major and minor species, trend analyses of PMF factor contributions should be more meaningful; in addition, PMF contributions (by definition) sum to unity on a per-sample basis. We next extend the trend analyses to examine source contributions apportioned using receptor modeling.

3.3. Long term source apportionments

The final PMF model for Detroit had nine factors with 5% additional model uncertainty, and the final model for Chicago had eight factors with 0% additional model uncertainty (Fig. 4). This number of factors and the (small) uncertainty additions (in Detroit) yielded factors that were interpretable and comparable to those in the literature, and both models closely matched $PM_{2.5}$ observations (Detroit: $R^2 = 0.96$; Chicago: $R^2 = 0.90$). Sources associated with each factor, which have been identified in previous apportionments (Gildemeister et al., 2007; Rizzo and Scheff, 2007), included secondary SO_4^- (characterized by SO_4^- and NH_4^+), secondary NO_3^- (NO_3^- and NH_4^+), vehicle emissions (EC for diesel vehicles and OC for gasoline vehicles), biomass burning (K+), industrial metal working (Ni, Cr, Mn, Fe), crustal sources (e.g., entrained soil as noted by Al, Si, Ca, Ti), and a zinc factor (which also can represent industrial emissions) (Gildemeister et al., 2007). While not unique tracers, OC and EC have been used to separate vehicle emissions into gasoline and diesel categories, respectively (Kundu and Stone, 2014); a factor containing both OC and EC can represent emissions from a mixed fleet. In the final models, a single factor contained moderate to high levels of both EC and OC, and thus the vehicle factor represents contributions from a mixed fleet.

The final PMF models using the full dataset gave nearly identical apportionments in Detroit and Chicago for the largest sources: sulfate formed 32–33% of $PM_{2.5}$; vehicles contributed 21–22%; nitrate constituted 21%; and biomass was 7–9%. These four sources represent over 80% of $PM_{2.5}$. Minor sources, e.g., crustal (4–8% of $PM_{2.5}$), several metals (4–11%) and Cl/NaCl (2–5%) showed greater variation, but accounted for relatively little $PM_{2.5}$ mass. The similarity of the apportionments for the major local sources (e.g., vehicles and biomass) is supported by the emissions inventory, e.g., the similarity of traffic emissions when expressed on an area basis; and the similarity of the secondary contributions (e.g., sulfate and nitrate) may reflect the same regional sources in these nearby cities (e.g., a large number of coal-fired power plants).

3.4. Source apportionment trends

The QR analysis of trends for the $PM_{2.5}$ PMF factors in Detroit is displayed in Fig. 5. These trends only roughly followed results seen for the major species in each factor (shown earlier in Fig. 2). Median concentrations of the secondary sulfate factor declined by 8.3%/yr, and seasonal changes were largest in fall and smallest in winter and summer. At the 90th percentile, sulfate factor concentrations declined slightly faster, 9.2%/yr overall, and declines were greatest in summer and smallest in winter. Changes in SO_4^- or NH_4^+ concentrations (dominant contributions to this factor) did not match the secondary sulfate pattern with the exception of the 90th percentile concentration change of NH_4^+. For the secondary nitrate factor, overall concentrations declined 7.0%/yr, and statistically significant decreases of 9.2–11.7%/yr occurred in spring, summer and fall (but not winter). This pattern (as well as the 90th percentile pattern) was not matched by NO_3^- and NH_4^+, this factor's major contributors. For the vehicle factor, decreases in median and 90th percentile factor concentrations were fairly consistent (2.8–5.2%/yr, depending on season) but dissimilar to trends in measured EC and OC. The biomass factor did significantly change over the study

period. Trends of factors representing the smaller $PM_{2.5}$ fractions may be less reliable for several reasons, e.g., PMF uncertainties (smaller factors are dominated by species with higher %BDL and thus higher associated uncertainties) and factor splitting (where changing the number of factors causes minor species to group in ways that may affect trends in minor factors). Still, several of the smaller components had statistically significant changes: the metals factor increased by 3.9 and 2.4%/yr for the median and 90th percentile, respectively; and the crustal factor declined by 5.8% and 3.3%/yr for the median and 90th percentile, respectively (the large decrease in winter was particularly notable).

The QR trend analysis for the Chicago PMF factors is depicted in Fig. 6. Median concentrations of the secondary sulfate factor decreased by 9.3 and 9.2%/yr for the median and 90th percentile, respectively; decreases were largest in summer. As in Detroit, these patterns differed from the trends of SO_4^- and NH_4^+ concentrations (Fig. 3). For the secondary nitrate factor, the only significant trends were decreases in the median concentrations in overall and in fall. Concentrations attributed to the vehicle factor did not change significantly. Few of the smaller factors at Chicago had statistically significant trends other than the median biomass contribution, which grew by 8.9%/yr due to large increases in spring and fall seasons.

A key result of this analysis is to show that $PM_{2.5}$ contributions from different sources have been evolving at different rates. In both cities, secondary sulfate has decreased faster than both the total $PM_{2.5}$ concentration as well as contributions of other factors identified by PMF, thus the relative significance of non-sulfate source factors increased over time. In particular, emissions from coal-fired facilities producing secondary sulfate and nitrate have been decreasing, while contributions from vehicle, biomass and metal (Chicago only) sources have been constant or just slightly declining. Given the trend of declining $PM_{2.5}$ levels, the vehicle, biomass and metal sources are becoming an increasing fraction of $PM_{2.5}$. Expressed as a percentage of the $PM_{2.5}$ concentration, the median contributions from secondary sulfate sources have decreased by 4.2–5.5% per year in Detroit and Chicago, while the contributions from metals sources, biomass sources, and vehicles have increased from 1.3 to 9.2% per year. (The Supplemental Information provides a discussion of seasonal factors and shows long term trends as Figs. S1 and S2 in the two cities.)

3.5. Vehicle apportionments and comparison to previous work

Many of the apportionment results described previously follow trends suggested by the emissions inventory and concentration data, and they also resemble previous apportionments in both cities conducted over the past 35 years. Here we examine those previous studies, focusing on vehicle apportionments given their significance as local emission sources in both cities.

In Detroit, using data from June through August of 1981 and a six source principal components model, vehicles accounted for 20% of the variability of $PM_{2.5}$ (Wolff et al., 1985). Vehicles accounted for 10–25% of $PM_{2.5}$ in a six factor PMF model using summer and early autumn data from 2000 to 2003 (Morishita et al., 2006). Using 2000 to 2005 data and a nine factor model, 21% of $PM_{2.5}$ in Detroit was attributed to vehicles (Rubin et al., 2006). Using the same data in an eight factor PMF model, gasoline and diesel vehicle contributions were separated with 15% and 4% apportioned, respectively (Gildemeister et al., 2007). That analysis did not include Ni or Cr, which may have affected the EC distribution between factors and changed results for diesel, and a lack of seasonality in the gasoline and vehicle factors was noted, contrary to the present findings (which used some of the same data). A recent analysis of 1999–2002 data attributed 22% of $PM_{2.5}$ to OC combustion sources
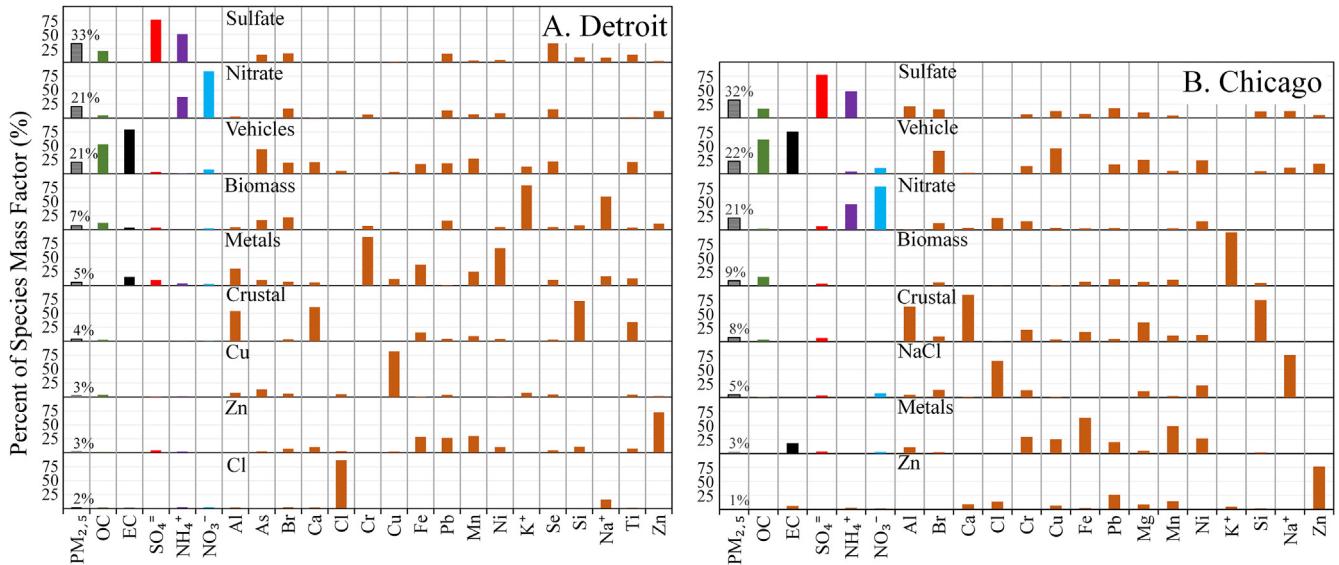
Fig. 4. Distribution of species by factor in PMF models for Detroit (A) and Chicago (B). Overall percentage contribution to modeled PM2.5 is listed for each factor.

and 15% to EC combustion sources in southwest Detroit, however, NO_3^- was not measured, potentially increasing the mass assigned to these factors (Hammond et al., 2008). Using August 2004 and July and August 2005 data, 29% and 8% of $PM_{2.5}$ was assigned to gasoline and diesel sources, and 31% to a combined gasoline and diesel fleet (Morishita et al., 2011). A recent Detroit area study, using 2004 to 2006 Allen Park data in a seven factor PMF model, attributed 22% of $PM_{2.5}$ to gasoline and diesel sources (Duvall et al., 2012). Using 2007 data from nearby Dearborn, Michigan, in an analysis incorporating wind direction, approximately 10% of $PM_{2.5}$ was apportioned to vehicles (diesel plus gasoline) (Pancras et al., 2013). Other apportionments cited in Michigan's $PM_{2.5}$ 2008 State Implementation Plan (Michigan Department of Environmental Quality (MDEQ), 2008b) showed vehicle apportionments comparable to the present study. Differences in samplers, species selected, length and seasons of the monitoring data used, and choices made in PMF modeling can diminish the comparability of these studies. Still, vehicle contributions in these earlier studies mostly ranged from 15 to 30% of $PM_{2.5}$, commensurate with the apportionments in the present analysis.

Several source apportionments have been performed in Chicago. Again, we focus on the vehicle component. In Northbrook IL (close to Chicago), using data from January 2003 to March 2005, 14% of $PM_{2.5}$ was apportioned to gasoline sources and 13% to diesel (Buzcu-Guven et al., 2007). The diesel profile included Al and Pb, elements assigned to other factors in the present study. Using 2001 to 2003 data at two CSN sites (Lawndale and Springfield, IL), 23% of $PM_{2.5}$ was apportioned to a combined vehicle profile (Rizzo and Scheff, 2007). That apportionment included both $SO_4^=$ and SO_2 (26), as well as both ionic and molecular forms of Na, Na^+, K and K^+. Despite these and other differences, the fraction of $PM_{2.5}$ attributed to gasoline and diesel vehicles in Chicago studies compare favorably to our estimates.

Vehicle apportionment trends have been studied elsewhere in the U.S. In Los Angles and Rubidoux, CA, a recent analysis using 2002 to 2013 STN data apportioned 20% of $PM_{2.5}$ to vehicles, and median $PM_{2.5}$ concentrations attributed to vehicles fell 21–24% between the first and last 4 year blocks of the study (Hasheminassab et al., 2014). Vehicle-related $PM_{2.5}$ decreased while traffic volume was stable, suggesting the success of recent vehicle emissions controls. Like the present work, that study shows

the relevance of receptor modeling apportionments for air quality management, as well as the evolution of source contributions to total $PM_{2.5}$. In contrast, we show that the share of $PM_{2.5}$ due to vehicle-, biomass- and other local emissions is stable or growing, and that trends depend on the city, percentile, and sometimes season (Figs. S1 and S2).

3.6. Limitations

Limitations of the analysis are recognized. Emission inventory data at the county level may not reflect the impact at monitoring sites, which can be affected by small but nearby sources, as well as large but distant sources (including sources outside county and country borders). A number of issues with the accuracy and consistency of the emissions inventory data were highlighted, e.g., fugitive dust emissions estimates are highly uncertain. The monitoring record is limited in both the duration and the number of sites available. Only two cities, and a single site in each, were examined. (Previous work has shown spatial trends in several $PM_{2.5}$ species (Simon et al., 2005)). However, the selected non-source and population-oriented monitoring sites should be reasonably representative. As noted, monitoring data near strong sources would be expected to show different trends for some $PM_{2.5}$ constituents as well as different apportionments, however, secondary sulfate, secondary nitrate, and potentially the vehicle contribution might not change greatly since these pollutants are widely distributed. The EC and OC instrument switch complicated the investigation of trends, particularly for mobile sources given the importance of these tracers. Still, most results follow national trends, and thus results appear broadly applicable to many U.S. cities.

The PMF analyses have additional limitations. First, results can be sensitive to the number of factors, species selected, and the data subset used. In sensitivity analyses, separate PMF models for individual four year blocks obtained average apportionments that were similar to those using the final model (across all years), but some trends were difficult to compare because factors varied across models. (Still, separate PMF models used for periods before and after the EC/OC instrument switch returned similar vehicle apportionments in models using different number of factors.) For these reasons, the current analysis used a single dataset that encompassing the entire study period. Second, trend analyses of
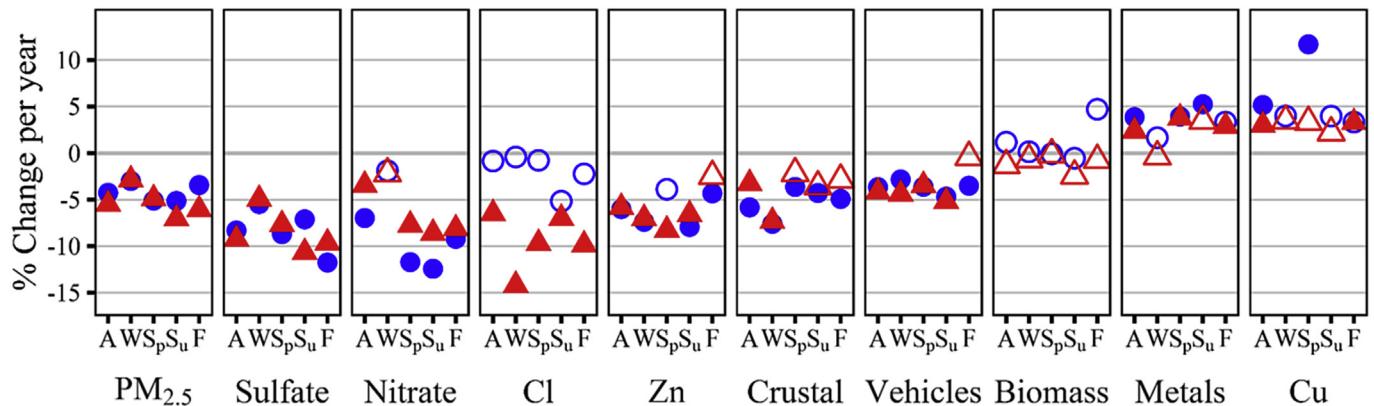
Fig. 5. Annual and seasonal trends of PMF apportionments by source category in Detroit from 2001 to 2014. Shows changes in median concentrations as blue circles (●, o) and 90th percentile concentrations as red triangles (▲, ∆), expressed as %/yr for all seasons (A), winter (W), spring (S_p), summer (S_u), and fall (F). Based on quantile regressions of estimated concentration apportionments from nine factor PMF model. Filled symbols (e.g., ●) are statistically significant, i.e., trend exceeded 2-times its bootstrapped standard error. Values below 0 not censored. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
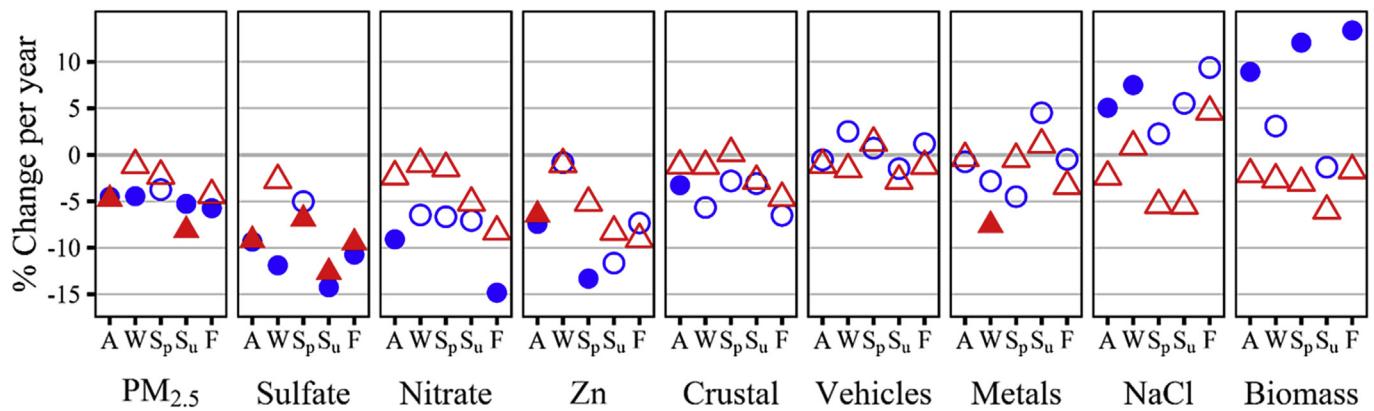
Fig. 6. Annual and seasonal trends of PMF apportionments by source category in Chicago from 2006 to 2014 using an 8-factor model. Otherwise as Fig. 5.

PMF results can be sensitive to the model selected. The stability of PMF results was investigated using 200 bootstrapped runs for each factor. In over 180 of 200 bootstrap runs at each city, the same factors emerged that are presented in these results. (Additional bootstrap results are presented in supplemental tables.) Third, PMF apportionments may not uniquely identify or completely characterize source classes, e.g., many factors might contribute to secondary sulfate trends. Similarly, unspecified minor sources and secondary pollutants can contribute to factors. Fourth, data screening can affect results, particularly for species near the DL. Fifth, PMF trend analyses may incorporate some biases because observations were removed by the reconstructed mass criterion. However, only 7% of sampling days at Detroit, and 6% at Chicago, were removed. Sixth, we did not apply conditional probability functions (CPF), which might provide additional qualitative information regarding the strength of local sources that complements the PMF results (Ashbaugh et al., 1985). Finally, the QR results do not account for the uncertainty of the PMF results, and thus determinations of statistical significance are approximate.

3.7. Recommendations

This study reports on trends and apportionments using a long record of emissions and ambient monitoring data from two cities. Analyses were constructed to provide consistent results, to combine emissions and ambient data, and to focus on contributions from both regional and local sources. While several differences between the two cities were noted, most trends were consistent and supported by both emissions and ambient data, as well as the PMF source apportionments. Such trends can inform air quality regulation and policy, including the formulation and implementation of emission and ambient standards, which in turn can lead to emission controls, new technologies, and promotion of cleaner fuels, among other options. These responses are most effective when emission sources can be clearly defined and apportioned. However, this approach may not adequately protect vulnerable populations given recent trends, including decreasing concentrations of regional and national pollutants (US EPA, 2014d)), increasingly indistinct profiles and identifications of local emission sources, the significance of secondary pollutants, and the still nascent understanding of health impacts associated with low concentration exposures and pollutant mixtures. A better understanding of emissions, ambient concentrations and source apportionments is required to reduce pollutant exposure and health impacts. The integration of source- and receptor-oriented apportionments, utilized in the present analysis, can enhance the ability to tease out contributions of sources for targeted interventions.

Future analyses may be strengthened in several ways. First, analyses might be stratified by climatic or meteorological variables to better account for seasonal factors than calendar-based periods, and to better separate trends in primary and secondary components (Ashbaugh et al., 1985). Second, weekday/weekend

groupings may reveal additional trends and better discriminate sources, particularly since truck traffic decreases significantly on Sundays (Batterman et al., 2015). Similarly, there may be opportunities to stratify by wind direction and other meteorological factors, although the duration (24 h) and frequency (every third day) of the CSN measurements may prove limiting. Third, hourly speciation measurements and stratification of PMF results by wind direction may improve the ability to identify sources (Rubin et al., 2006). Fourth, comparisons of factor contribution on high and low pollution days might help distinguish contributions of local sources, e.g., traffic-related air pollutants (Adamski et al., 2009). Fifth, while emissions trends can be tracked for some sources, greater consistency in methods and source grouping across years would improve long-term studies. In particular, emissions data for crustal, fugitive, metals and biomass sources is highly uncertain. Sixth, regional emission inventories might be examined to help confirm changes in regional contributors of secondary sulfate and nitrate. Finally, applications of long term trend analyses to other cities would be help confirm trends.

4. Conclusions

The changing contribution of $PM_{2.5}$ sources is shown by long term trends in $PM_{2.5}$ emissions, concentrations and PMF source apportionments in Detroit and Chicago. In both cities, $PM_{2.5}$ levels have been declining, primarily due to reductions in secondary sulfate and, to a more limited extent, in nitrate sources, while the importance of emissions due to vehicles, biomass, and metals sources is increasing. This is supported by examining three data sources: county emission data, which show constant or declining emissions from point sources and slightly increasing or constant emissions from on-road mobile sources; ambient monitoring data, which show rapid declines in SO_4^- and NO_3^- concentrations, but steady or increasing abundances of OC and EC, tracers for gasoline and diesel vehicle exhaust; and receptor model results, which show increasing relative (percentage) contributions from these sources. Quantile regression estimates of PMF results, expressed as the %/yr change in the annual median relative contribution to total $PM_{2.5}$ over the study period, show that the contribution from secondary sulfate decreased by 4.3—5.5%/yr, while vehicle, biomass and metals source contributions increased by 1.3—9.2%. In most cases, the rate of change depends on the season and concentration percentile.

The study has several unique aspects. Trends in emissions and ambient data, which provide complementary information, are compared and critiqued. The PMF application covered an extended period (up to 14 years), which allowed for analyses of annual and seasonal apportionment trends. Also novel is the determination of concentration and apportionment trends using quantile regression, a method that provides robust results.

The study's key finding that, in both cities, the mobile source, biomass, and metal source contributions to $PM_{2.5}$ have increased even as overall $PM_{2.5}$ concentrations have declined, has significant implications for air quality management. It emphasizes the need to investigate these sources in policies and regulations aimed at maintaining or decreasing $PM_{2.5}$ concentrations.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.01.012.

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