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# Composition and sources of fine particulate matter across urban and rural sites in the Midwestern United States

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## Environmental Impact Statement

Atmospheric particulate matter presents risk to human health and contributes to mortality and morbidity.  Improvement of air quality requires understanding the nature of pollution sources.  In this study, the chemistry and sources of fine particulate matter in airsheds over urban and rural sites in Iowa were quantitatively evaluated with source apportionment modeling.   Significant enhancements in diesel and gasoline vehicular and industrial sources were found in urban areas, while biomass burning was enhanced in rural areas. Particulate matter from secondary sources was consistent in concentration across the urban-rural continuum, leading to the conclusion that they are controlled by regional atmospheric processes rather than local sources.  Efforts to improve air quality will require targeting different primary sources in urban and rural areas.

## Abstract

The composition and sources of fine particulate matter ($PM_{2.5}$) were investigated in rural and urban locations in Iowa, located in the agricultural and industrial Midwestern United States from April 2009 to December 2012. Major chemical contributors to $PM_{2.5}$ mass were sulfate, nitrate, ammonium, and organic carbon. Non-parametric statistical analyses demonstrated that the two rural sites had significantly enhanced levels of crustal materials (Si, Al) driven by agricultural activities and unpaved roads. Meanwhile, the three urban areas had enhanced levels of secondary aerosol (nitrate, sulfate, and ammonium) and combustion (organic and elemental carbon). The heavily industrialized Davenport site had significantly higher levels of $PM_{2.5}$ and trace metals (Fe, Pb, Zn), demonstrating the important local impact of industrial point sources on air quality. Sources of $PM_{2.5}$ were evaluated by the multi-variant positive matrix factorization (PMF) source apportionment model. For each individual site, seven to nine factors were identified: secondary sulfate (accounting for 29-30% of $PM_{2.5}$), secondary nitrate (17-24%), biomass burning (9-21%), gasoline combustion (6-16), diesel combustion (3-9%), dust (6-11%), industry (0.4-5%) and winter salt (2-6%). Source contributions demonstrated a clear *urban* enhancement in $PM_{2.5}$ from gasoline engines (by a factor of 1.14) and diesel engines (by a factor of 2.3), which is significant due to the well-documented negative health impacts of vehicular emissions. This study presents the first source apportionment results from the state of Iowa and is broadly applicable to understanding the differences in anthropogenic and natural sources in the urban-rural continuum of particle air pollution.

## 1. Introduction

Air pollution presents a major health risk and contributes to acute and chronic disease including respiratory infections, heart disease, and cancer.[1, 2] Respirable particulate matter (PM) has a greater impact on human health outcomes than other ambient air pollutants, including ozone, sulfur dioxide, and nitrous oxides.[3] Decades of epidemiological have documented the association between exposure to ambient $PM_{10}$ and mortality. For example, mortality was strongly and significantly correlated with increases in daily $PM_{10}$ concentrations in the urban area of St. Louis, Missouri and in surrounding communities.[3] A study covering twenty cities in the United States (US) established the connection between elevated $PM_{10}$ and cardiovascular and respiratory illnesses, in particular.[4] Within a region, the health effects of aerosols measured *in vitro* by cytotoxicity, inflammation, and oxidative stress endpoints differ across urban, rural, and remote locations due to differences in PM composition and sources.[5] Due to this underlying connection between ambient PM and health, the United States Environmental Protection Agency has established National Ambient Air Quality Standards (NAAQS). The primary standard for $PM_{2.5}$ on an annual average basis was set at 15 μg $m^{-3}$ in 1997 and was reduced to 12 μg $m^{-3}$ in 2012.[6]

Particulate mass has historically been the metric for regulation, because its relationship to health effects is well documented. However, the majority of the particle mass is comprised of low-toxicity minerals derived from soil dust and inorganic salts like ammonium sulfate, ammonium nitrate, and sodium chloride.[7] Transition metals that have low atmospheric abundance, but are capable of redox cycling, contribute significantly to adverse health effects.[8-10] Thus, the chemical composition of PM is expected to be an important determinant in its health outcomes.

Reductions in ambient $PM_{2.5}$ are consistent with longer life expectancies, yet the benefits of PM reductions are greater in urban areas in comparison to rural areas.[11] Rural locations are inherently understudied, although 19.3% of Americans, or over 59 million people in the United States live in rural communities.[12] This percentage is much higher in Midwestern states such as Iowa where 43.5% of the population lives in rural areas.[13] Spatial differences in PM composition are driven by different sources across urban and rural locations. Toxic metal levels are enhanced in polluted urban and industrial locations[3, 4] and near-roadways.[14, 15] In agricultural areas bioaerosols are generated by harvesting, transporting, processing, or storing grain, and livestock operations and these bioaerosols enriched in biological material of microbial, plant, or animal origin[16] and are typically greater than 2.5 μm in diameter.[17] Dusts in agricultural areas can be distinguished from urban dusts by their metal composition.[16, 18] Urban dusts generally contain higher concentrations of metals emitted from industry and vehicles,[18, 19] whereas agricultural dusts are more enriched in crustal metals.[16]

Receptor-based source apportionment modeling is a technique used to evaluate the sources of pollution and to maintain air quality standards.[20] Positive matrix factorization (PMF) is a receptor-oriented source apportionment model which can resolve factors, factor profiles and factor contributions to ambient measurements.[21] PMF analyzes the co-variation of chemical species over time and identifies factors based on a constrained weighted least-squares matrix.[21, 22] PMF has been successfully used as a source apportionment tool of $PM_{2.5}$ in many air quality studies in the USA.[23-26] Prior PMF studies in the USA have resolved in the range of 7-11 sources at different locations, including secondary sulfate, secondary nitrate, wood combustion, and fossil fuel (gasoline, diesel and coal) combustion and minor sources such as dust, sea salt, and point sources. While these prior studies have focused on one or two receptor locations, there is need to understand the differences in PM sources across broader spatial scales and understand the differences in PM composition across urban and rural locations.

This study investigates the composition and sources of $PM_{2.5}$ across urban and rural locations in the agricultural and industrial Midwestern United States. Using measurements of $PM_{2.5}$ from three cities in Iowa and two background locations obtained from USEPA Air Quality Database (USEPA AQS Data Mart), seasonal and spatial differences were investigated with statistical methods and $PM_{2.5}$ sources were evaluated with PMF modeling. This study presents the first source apportionment of $PM_{2.5}$ in Iowa. With a focus on = quantifying regional and local pollution sources, we present new information on the spatial variability in PM composition and sources across the rural-urban continuum.

## 2. Material and methods

### 2.1. Sampling sites, aerosol sampling and chemical analysis

Five USEPA $PM_{2.5}$ monitoring sites in Iowa were considered in this study (Fig. 1). Cedar Rapids (42.0051° N, 91.6793° W), Des Moines (41.6032° N, 93.6431°W), and Davenport (41.5300° N, 90.5876° W) are cities with populations (and number of houses) of 126,326 (57,217), 203,433 (88,729), and 99,685 (44,087), respectively.[27] These three urban sites are part of the EPA Chemical Speciation Network (CSN). Rural sites included Viking Lake State Park in Montgomery County (40.9691° N, 95.0450° W) and Lake Sugema State Park in Van Buren county (40.6951° N, 92.0063° W), where populations (and numbers of houses) are 10,740 (5,239) and 7,570 (3,670), respectively.[27] These two sites are part of the EPA Interagency Monitoring of Protected Visual Environments (IMPROVE) network. During the spring and summer, winds are predominantly southerly and north-westerly at the study sites. During winter and fall, winds are predominately north-westerly. It is important to note that summertime southerly winds may transport air masses from the St. Louis, MO urban area to the rural Van Buren site and westerly may transport air masses from the Omaha, NE urban area to the Montgomery site.

All aerosol samples were collected and analyzed by the United States EPA; all data analyzed in this study were retrieved from the AQS Datamart.[6] Details of sample collection and filter analysis are described in detail elsewhere.[28] Briefly, PM samples were collected using commercial air samplers. $PM_{2.5}$ mass concentrations were measured gravimetrically on Teflon filters. Elemental composition was measured by the energy dispersive X-ray fluorescence (EDXRF) on Teflon filters for Na, K, Al, Ca, Mg, Si, Ti, Zr, Rb, Sb, Fe, Cr, Cu, Zn, Mn, Pb, As, Br, Cl, Se, Ni, V, Cd and Sr. Water-soluble inorganic ions ($SO_4^{2-}$, $NO_3^-$ and $NH_4^+$) were measured by ion chromatography on either nylon or Teflon filters; however, $NH_4^+$ data were not available for Montgomery and Van Buren. Fractions of organic carbon (OC1, OC2, OC3 and OC4) and elemental carbon (EC1, EC2, and EC3) were measured using the thermal-optical OC/EC analyzer (DRI Model 2001) on quartz fiber filters.[29] Organic carbon was operationally-defined into four fractions evolving at 120 °C, 250 °C, 450 °C and 550 °C, respectively whereas elemental carbon was defined by three fractions evolving at 550 °C, 700 °C and 800 °C, respectively.[30] Thermal optical reflectance (TOR) was used to account for the conversion of OC to pyrolytic organic carbon (OP) during the thermal gradient.[31] The EC1 fraction was corrected for OP and is denoted EC1-OP.

Sample data were drawn from April 2009 to December 2012 after the CSN and IMPROVE networks adopted consistent methods of sample collection and analysis, ensuring data are comparable across networks. The Cedar Rapids and Des Moines sites followed the one-in-six day sampling frequency whereas Davenport and rural locations followed the one-in-three day sampling frequency. Sample data from 3-5 July were excluded because of outlying concentrations of trace metals and potassium, due to fireworks and local activities, which biased results. For the discussion of seasonal variations, winter is defined as December-February, spring as March-May, summer as June-August, and fall as September-November.

### 2.2. Statistical analysis of data

$PM_{2.5}$ mass and speciation data were analyzed using the Statistical Package for the Social Sciences (SPSS) software (version 21) in order to evaluate the statistical significance of differences (at the 95% confidence interval) in PM mass and species concentrations across the study sites. The Kolmogorov-Smirnov and Shapiro-Wilk tests indicated that chemical speciation data was not normally distributed and the Levene test indicated that there was no homogeneity of variance (homoscedasticity) in the data.[32] Consequently, non-parametric statistical tests (i.e. the U of Mann Whitney and the Z of Kolmogorov-Smirnov) were used.[32]

### 2.3. PMF analysis and modeling parameters

Positive matrix factorization (EPA PMF version 3.0) is a multivariate factor analysis tool that decomposes a matrix X (n × m) of chemically-speciated samples into two matrices including source contributions (G, n × p) and source profiles (F, p × m),[21] for number of samples (n), number of chemical species (m), and the number of factors (p).[33] PMF ensures that all of the species profiles (matrix F) are non-negative, each sample has a non-negative source contribution (matrix G), and the sum of the predicted elemental mass contributions for each source must be less than or equal to the total measured mass for each element. The mass balance equation (1) in the PMF can be written in the following way:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where $x_{ij}$ is the concentration of $j^{th}$ chemical species in the i number of samples, $g_{ik}$ is the mass concentration in the $i^{th}$ sample from the $k^{th}$ source, $f_{kj}$ is fraction of chemical species j from the source k, and $e_{ij}$ is the residual of species j in the $i^{th}$ sample.

PMF allows the adjustment of each data point based on the uncertainty measurements. In this way, the influence of data points with lower or more uncertain concentrations can be minimized. The PMF uncertainty function is

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}}\right]^2 \qquad (2)$$

where $u_{ij}$ is the user defined uncertainty in the $j^{th}$ species for $i^{th}$ sample. The PMF model solves for the Q minima using the input provided by the user to the program.[33]

In this study, $PM_{2.5}$ mass concentrations were supplied as the total variable[34] and fitting species included OC1, OC2, OC3, OC4, EC1-OP, EC2, EC3, OP, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, Na, K, Al, Ca, Mg, Si, Ti, Zr, Rb, Fe, Cr, Cu, Zn, Mn, Pb, As, Br, Cl, Se, Ni, V, Cd and Sr, when data met the model criteria.[35] If the 80% of data of a chemical species were below detection limit, data were not considered. Data were processed following the recommendations of Polissar et al.[36]. The uncertainty input to the model was the sum of the measurement uncertainty and one-third of the method detection limit (MDL), both supplied by the AQS Data base.[6] When the measured concentrations fell below the MDL, the data were replaced by 1/3 of MDL and their uncertainties were assigned as 5/6 of MDL. Species were then categorized following the recommendations of Paatero and Hopke.[37] If the signal to noise ratio for a chemical species was less than 2, the uncertainty of the data were increased by three times. If the signal to noise ratio was less than 0.2, the data were not considered.

The "base run" was executed with different factor solutions to find the global minima Q.[36] The stability and uncertainty of the base PMF results with the lowest Q value were analyzed by bootstrapping and Fpeak analysis, respectively.[38] In the bootstrapping stage, the PMF model synthesized new datasets from non-overlapping block of samples; 95-100% of the bootstrapped factors were mapped to the corresponding base factor and the concentrations of dominant species in the base solution were within the interquartile range of the bootstrapped factors, both indicating stable model result. Across the base run and five Fpeak analyses (ranging -1 to +1), neither significant changes in calculated Q-values nor significant changes in factor contributions were observed. The error in factor profiles was determined as the standard deviation of the base result and the Fpeak result at a strength of 0.5.[38]

## 3. Results and discussion

### 3.1. Spatial variability of $PM_{2.5}$

Annual-average $PM_{2.5}$ concentrations across the five study sites are shown in Figure 2. In general, rural locations generally exhibited lower $PM_{2.5}$ concentrations (8.4-10.4 $\mu g\ m^{-3}$) compared to the urban sites (9.5-11.6 $\mu g\ m^{-3}$). Non-parametric statistical analyses demonstrate that Davenport $PM_{2.5}$ loadings are significantly higher ($p < 0.005$) than the other four sites, while $PM_{2.5}$ mass concentrations were not significantly different across Cedar Rapids, Davenport, Montgomery, and Van Buren (Table 1). Annual average $PM_{2.5}$ concentrations exceeded neither the primary EPA NAAQS of 15 $\mu g\ m^{-3}$ set in 2006 nor the revised primary standard of 12 $\mu g\ m^{-3}$ set in 2012.[39] The study sites were also in compliance with the 24-hour average $PM_{2.5}$ NAAQS standard of 35 μg $m^{-3}$. The elevated $PM_{2.5}$ levels in Davenport are driven by local activities and are discussed in the context of chemical tracers section 3.2.

### 3.2. Seasonal and spatial variations of chemical components in $PM_{2.5}$

Monthly-averaged concentrations of $PM_{2.5}$ species are shown in Figure 3, including secondary ions ($NH_4^+$, $NO_3^-$, $SO_4^{2-}$), organic carbon (OC), elemental carbon (EC), crustal elements (Si, Ca, Al) and trace metals (Fe, Pb, Zn and Cu) and demonstrate significant differences across urban and rural areas.

Crustal elements (Si, Ca, Al) are elevated in spring, summer, and fall periods and lowest in winter. The seasonal variation is driven by groundcover, seasonal differences in agricultural activities, and long-range transport.[26, 40] The monthly averaged Si concentrations at the two rural sites ranged 0.02-0.36 μg $m^{-3}$ and were significantly higher ($p < 0.039$) than urban concentrations (0.01-0.24 μg $m^{-3}$) (Table S1). Likewise, Al concentrations at rural sites were ranged from 0.10-0.13 μg $m^{-3}$ were significantly higher ($p < 0.031$) compared to urban site levels of 0.07-.08 μg $m^{-3}$ (Table S1). The enrichment of crustal metals at rural sites indicates a greater influence of resuspended dusts on $PM_{2.5}$ in rural locations.

Urban locations had enhanced concentrations of trace metals, particularly those associated with industrial activity. Average urban levels of Fe, Pb, and Zn ranged from 0.04 – 0.07 μg $m^{-3}$, 0.001 – 0.005 μg $m^{-3}$, and 0.006 – 0.011 μg $m^{-3}$ while average rural concentrations were 0.03-0.04 μg $m^{-3}$, 0.002 μg $m^{-3}$, and 0.006 μg $m^{-3}$, respectively. Maximum trace metal concentrations were observed at Davenport, where heavy industry includes manufacturing of agricultural machinery, heavy weapons, and ammunition, and associated truck and ship traffic. Statistical analysis (Table S2) shows that Davenport metal data are significantly different from the rural and other two urban sites ($p < 0.001$). With the exception of Zn, the Cedar Rapids and

Davenport sites are also statistically different from the rural sites. These data provide conclusive evidence of enhanced exposure to toxic elements in urban areas of heavy industry compared to rural locations.

Organic carbon is derived primary combustion sources (such as biomass burning or fossil fuel use) as well as secondary organic aerosol (SOA formation). OC was a dominant component of $PM_{2.5}$ contributing 2.3-67.3% of $PM_{2.5}$. Daily OC concentrations ranged from 0.3-5.2 $\mu g\ m^{-3}$ at urban sites compared to 0.1-4.6 $\mu g\ m^{-3}$ at the rural sites. OC levels were significantly elevated at urban sites compared to rural locations ($p < 0.001$). Also, OC concentrations were significantly different between Davenport and other two urban locations ($p < 0.043$; Table S1). These results are consistent with prior studies that reported urban enhancements of OC levels in the range of 2-5 compared to rural sites in the US.[40, 41] These data reveal the importance of local sources of carbonaceous aerosol loadings in urban areas and that OC loadings are reduced in rural areas.

Elemental carbon is the product of incomplete combustion of carbonaceous material and is considered a tracer for diesel engine emissions.[42] Like OC, EC levels were enhanced in urban areas with average concentrations of 0.03-1.5 $\mu g\ m^{-3}$ compared to rural sites with average concentrations of 0.01-1.0 $\mu g\ m^{-3}$. EC levels are significantly enhanced in urban locations ($p < 0.001$), indicating the greater role of combustion-derived PM in urban airsheds.

Secondary ammonium nitrate ($NH_4NO_3$) is a major contributor to $PM_{2.5}$ across urban and rural locations. Secondary sources are generally considered to be regional in nature. The monthly average $NO_3^-$ and $NH_4^+$ concentrations have similar seasonal variations and are well-correlated ($r^2 = 0.79$-$0.85$) across the five study sites. The highest $NO_3^-$ concentrations were recorded in winter (4.1-5.0 $\mu g\ m^{-3}$) and lowest in summer (0.2-0.5 $\mu g\ m^{-3}$). Likewise, The $NH_4^+$

concentration was lowest in in summer (0.5-0.7 µg $m^{-3}$) and peaked during winter (1.9-2.0 µg $m^{-3}$). It is well-established that winter conditions (including long nights, lower temperatures and boundary layer height, and higher humidity) promote the formation of secondary $NH_4NO_3$.[43, 44] The summertime minimum may be partially enhanced to negative sampling artifacts whereby ammonium nitrate volatilizes as ammonia and nitric acid from Teflon filters during periods of elevated temperatures.[45] These seasonal variations of $NH_4^+$ and $NO_3^-$ are consistent with a greater trend across the US.[46, 47] The daily concentrations of $NO_3^-$ were statistically different ($p < 0.011$) between rural and urban locations (except for Des Moines) (Table S1). Higher $NO_3^-$ concentrations in the urban atmospheres are associated with the higher amount of $NO_x$ emissions from the combustion sources, particularly automobiles.[40] The daily concentrations of $NO_3^-$ are also significantly different between urban sites, indicating the importance local combustion contributions to $NO_3^-$.

Secondary $SO_4^{2-}$ was a major contributor to $PM_{2.5}$ mass, but showed little seasonal variation, at levels ranging from 1.5-2.1 µg $m^{-3}$ in spring, 1.7-2.7 µg $m^{-3}$ in summer, 1.3-1.7 µg $m^{-3}$ in fall and 1.6-2.2 µg $m^{-3}$ in winter (Fig. 3c). Similar concentrations have been reported for the rural and urban areas in the central US, Central Great Plains, and Northeastern US.[40, 41, 48] Daily $SO_4^{2-}$ concentrations were significantly enhanced at Davenport (0.01-10.3 µg $m^{-3}$) when compared to Cedar Rapids (0.3-9.3 µg $m^{-3}$, $p < 0.003$), Des Moines (0.01-7.5 µg $m^{-3}$, $p < 0.003$) and the rural sites (Montgomery: 0.04 to 8.1 µg $m^{-3}$, $p < 0.001$, and Van Buren: 0.2 to 9.3 µg $m^{-3}$, $p < 0.001$, Table S1). Higher concentrations of $SO_4^{2-}$ at Davenport could be related to greater emissions of $SO_2$ from industry and boat-engines on the nearby Mississippi River, which burn fuels with higher sulfur content. The combination of secondary ion data demonstrates that local combustion contributes to atmospheric $SO_2$ and $NO_x$ contribute to local secondary aerosol, giving rise to spatial differences across the urban-rural continuum.

### 3.3. Source identification and factor profiles

With the expectation of differences across urban and rural areas, the PMF model was run separately for each study site. Base model results, with lowest Q value, are summarized in Table 2 and were obtained for a 9-factor solution for Cedar Rapids, an 8-factor solution at Des Moines, and 7-factor solutions for Davenport, Montgomery and Van Buren sites. Representative chemical profiles of PMF factors for the Cedar Rapids site are shown in Fig. 4. The left axis shows the log-transformed $PM_{2.5}$ mass fraction of each species, whereas the right axis shows the percent of species attributed to that factor. The factor contributions to ambient $PM_{2.5}$ across urban and rural sites are shown in Table 2.

The PMF model resolved factors that were common to all five sites: secondary sulfate, secondary nitrate, biomass burning, gasoline engines, diesel engines, and dust. Industrial factors were only resolved at the three urban sites. Winter salt, associated with the use of salt as a road deicer[23] was not resolved at the Des Moines site. At the Davenport site, diesel and gasoline engine factors were mixed with trace metals, suggestive of mixed engine and industrial factors, leading to a low industrial source contribution despite the greatest trace metal concentrations. Gasoline and diesel engine factors at the rural sites co-varied with road dust, giving rise to combined factors. Two dust factors, one enriched in Ca and the other in Al-Si were resolved at Cedar Rapids and were summed for discussion. It is also notable that the industrial factor at Des Moines included minor amounts of crustal elements (Al, Fe and Si). Varying the number of factors did not resolve these co-variances.

The first secondary sulfate (I) factor is characterized by high concentrations $SO_4^{2-}$ and $NH_4^+$ and accounted for 66-68% of the observed $SO_4^{2-}$ and 41-54% of the observed $NH_4^+$ (Fig. 4a, Table 2). A second secondary sulfate factor (II) with higher concentration of $SO_4^{2-}$ and carbonaceous fractions were also detected for Des Moines and rural sites, consistent enhanced SOA formation in the presence of sulfate.[49] This factor does not show any characteristic seasonal variation (Fig. 5a), although prior studies have documented summertime secondary sulfate production.[23] The secondary sulfate factor accounted for 30-44% of the $PM_{2.5}$ mass concentration at the urban and rural sites (Table 2). Similar contributions were also obtained for this source in some other rural and urban sites in the Midwest USA such as East St. Louis, IL; Detroit, MI; and Bondville, IL, [23, 25, 26] but were approximately half the level detected in the northeastern United States.[50] There was a modest enhancement by a factor of 1.08 in secondary sulfate at urban sites relative to rural locations.

The secondary nitrate factor is characterized by high concentrations of $NO_3^-$, accounting for 84-90% of observed nitrate (Fig. 4b). Seasonally, secondary nitrate peaked winter (Fig. 5b) when low temperatures and longer nights promote the formation of secondary $NH_4NO_3$.[43, 44] This factor accounted for 17-24% of $PM_{2.5}$ mass at the monitoring sites with maximum contributions occurring in winter (Table 2). A minor rural enhancement (1.03) in the secondary nitrate PMF factor was detected in PMF model results, but is not consistent with the urban enhancement in ambient nitrate concentrations. This anomaly is expected to be an artifact of missing $NH_4^+$ data at the rural sites. PMF-resolved secondary sulfate and nitrate factors account for a significant portion of ambient $PM_{2.5}$ loadings, indicating the important role of secondary aerosol in ambient PM in the Midwestern US.

The biomass burning factor was characterized by higher OC to EC ratio and K (Fig. 4c).[51-53] This factor showed no discernable seasonal variations or point source impacts (Fig. 5c). Although the nature of biomass burning varies seasonally, from home heating in the winter to open burning in the summer, these data suggest relatively consistent, year-round contributions to $PM_{2.5}$. The biomass burning factor made important contributions to $PM_{2.5}$, averaging 16% in Cedar Rapids, 9% in Des Moines, 16% in Davenport, 21% in Montgomery, and 12% in Van Buren (Table 2). The relative contribution of biomass to $PM_{2.5}$ in Iowa aerosols is several times higher than other Midwestern cities, including Detroit, MI; and Chicago and East St. Louis, IL, while it was not detected at a rural site in Bondville, IL.[23, 25, 26] Biomass burning contributions to $PM_{2.5}$ were slightly enhanced in rural locations (by a factor of 1.05) relative to urban sites.

The industrial emission factor is characterized by trace elements including Mn, Cr and EC1-OP along with Cu, Zn, Pb, Cl, As, Ni, and V (Fig. 4d).[23] Industrial contributions were not affected by season (Fig. 5d). The industrial emission accounted for 0.4-5% of $PM_{2.5}$ at urban sites, but was not resolved at rural sites. While industrial sources have impacts locally, they are observed not to have far-reaching consequences on air quality that lead to background levels of trace elements at the rural sites.

The gasoline engine factor was characterized by higher concentrations of OC and EC1 along with trace metal Zn (Fig. 4e). No seasonal variation was observed for gasoline engine factor (Fig. 5e), consistent with observations in the Detroit, MI.[23] The diesel engine factor was characterized by high concentrations of EC relative to OC. In addition, this factor had the greatest contributions to select metals (including Pb, Ni, V) (Fig. 4f).[30] However, the diesel engine factor exhibited summertime maxima (Fig 5f), which may be associated with vehicle-enhanced secondary organic aerosol (SOA) production. The combination of vehicular tracers with crustal elements indicates that gasoline and diesel engine factor incorporate non-tailpipe emissions and resuspended road dust. Prior source profiling efforts have reported Cu emissions from brake wear, Zn from the erosion of brake linings,[54] and Pb from resuspension of road dust [55]. The relative contributions of gasoline and diesel engines to $PM_{2.5}$ are reported in Table 2 and are consistent with prior source apportionment studies in the region for which motor vehicles accounted for 19% of $PM_{2.5}$ in urban East St. Louis, IL [26] and 11% of $PM_{2.5}$ at a rural monitoring site in Bondville, IL[25]. The PMF results demonstrate a substantial urban enhancement in diesel engine contributions to $PM_{2.5}$ (by a factor of 2.29) and gasoline vehicles (by a factor of 1.14), which is significant due to the toxic and carcinogenic properties of vehicular emissions.[56]

Two soil factors were resolved (Figs. 4g, h), with one enriched in Ca, Mg and Si (termed Ca-enriched dust) and the other enriched in Al and Si (termed Al-enriched dust). Together, these factors explain majority of the observed crustal elements (Ca: 83%, Al: 92% and Si: 80%). Both soil factors exhibit maxima in spring and fall which seasonally coincide with planting and harvesting of agricultural lands (Figs. 5g, h), however fine-scale temporal differences are responsible for the two separate factors that likely have different geological origins. Together, the two dust factors accounted for 6-11% of $PM_{2.5}$ concentrations in urban locations and 6% of $PM_{2.5}$ concentrations in rural locations. Lower contributions at rural sites are due to the inclusion of road dusts with vehicular factors. These results are consistent with prior studies that reported $PM_{2.5}$ dust contributions of 4% at a rural location at Bondville, IL and 4-8% in urban areas at Detroit, MI.[23, 24]

The winter salt factor was characterized by maximum concentrations of Na or Cl (Figure 4i) and maximum contributions in the wintertime (Figure 5i), which coincides with the use salt to deice roadways. This factor contributed to 2-3% of $PM_{2.5}$ at urban locations and 4-6% of $PM_{2.5}$ at rural locations, consistent with prior studies that report this source contributing 5-8% of $PM_{2.5}$ contribution in the US.[23, 24]

Representative chemical profiles of PMF factors at a rural site (Van Buren) are shown in Fig. S1. Seven factors were identified following the almost similar approach described above: secondary sulfate (38% of $PM_{2.5}$), secondary nitrate (22%), biomass burning (12%), gasoline combustion (13%), diesel combustion (3%), dust (6%), and winter salt (6%). Minor differences were observed between the gasoline and diesel factors for the Cedar Rapids and Van Buren sites. Both gasoline factors were characterized by OC and EC1 and Zn, with a stronger road dust influence at the Van Buren Site. Both diesel factors were enhanced in EC relative to OC and contained Pb, Ni, V and other trace metals. In addition, the diesel factor at Van Buren included higher mass fractions of Ca and Mg, which is caused by the covariance of diesel emissions and resuspended dust in rural locations.

## 4. Summary and Conclusions

This study elucidates differences in $PM_{2.5}$ composition and its sources at three urban locations—Cedar Rapids, Des Moines, and Davenport—and two rural locations—Montgomery and Van Buren Counties—in Iowa. Air quality in the heavily industrial city of Davenport is worse than other locations in terms of $PM_{2.5}$ loadings and higher levels of trace metals, including Fe, Zn and, Pb, which demonstrate the important role of local industrial activity in urban air quality. Significant differences in OC and EC loadings, biomass burning contributions, and vehicular sources across urban and rural sites are driven by local emissions. These local emissions also give rise to spatial differences in secondary sulfate and ammonium nitrate across the urban-rural continuum. Higher levels of crustal elements (Ca, Al and Si) at Montgomery and

Van Buren sites demonstrate the importance of wind-blown soil and dust in rural air quality, that are driven by agricultural activities and unpaved roadways in rural environments.  This study demonstrates that regional efforts are needed to reduce secondary PM in the Midwestern USA with incremental benefits from local reductions.  Meanwhile, local pollution controls on industry, vehicles, and biomass burning are needed to improve urban air quality. Reductions in PM loadings will require targeting different sources in urban and rural areas.

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**Table 1.** Statistical significance (p-value) of the non-parametric tests of U of Mann-Whitney (upper matrix) and Z of Kolmogorov-Smirnov (lower matrix) tests for $PM_{2.5}$ mass. Results in bold correspond to significant differences between the two sites (i.e. the null hypothesis is rejected) with $p > 0.05$.

| Sites | Cedar Rapids | Des Moines | Davenport | Montgomery | Van Buren |
|---|---|---|---|---|---|
| Cedar Rapids | | 0.861 | **0.005** | 0.810 | 0.596 |
| Des Moines | 0.779 | | **0.001** | 0.962 | 0.771 |
| Davenport | **0.008** | **0.002** | | **0.001** | **0.001** |
| Montgomery | 0.326 | 0.296 | **0.001** | | 0.706 |
| Van Buren | 0.785 | 0.907 | **0.001** | 0.768 | |

**Table 2.** Absolute and relative contributions of PMF factors to $PM_{2.5}$ at urban and rural sites in Iowa.

| **Source** | **Source characteristics** | **Contribution in μg $m^{-3}$ (%)** | | | | | ***Enhancement factor*** | |
|---|---|---|---|---|---|---|---|---|
| | | **Cedar Rapids** | **Des Moines** | **Davenport** | **Montgomery** | **Van Buren** | ***Urban*** | ***Rural*** |
| Secondary sulfate | $SO_4^{2-}$, $NH_4^+$, OC | 2.7 (30) | 3.1 (44)[a] | 3.2 (31) | 3.0 (35) | 3.2 (38) | 1.08 | - |
| Secondary nitrate | $NO_3^-$, $NH_4^+$ | 2.1 (23) | 1.5 (17) | 2.1 (21) | 2.1 (24) | 1.8 (22) | - | 1.03 |
| Biomass burning | K, OC | 1.5 (16) | 0.9 (9) | 1.6 (16) | 1.8 (21) | 1.0 (12) | - | 1.05 |
| Gasoline combustion | OC, EC1, Zn | 0.5 (6) | 0.7 (7) | 1.7 (16)[b] | 0.5 (6)[c] | 1.2 (13)[b] | 1.14 | - |
| Diesel combustion | EC2, OC, Pb | 0.9 (9) | 0.6 (7) | 0.9 (8) | 0.4 (5) | 0.3 (3)[b] | 2.29 | - |
| Dust | Si, Al, Ca, Fe, Ti | 0.9 (11)[d] | 1.0 (11) | 0.6 (6) | 0.5 (6) | 0.5 (6) | 1.67 | - |
| Industry | Mn, Cr, Cu, Ni | 0.4 (4) | 0.4 (5) | 0.04 (0.4)[b] | - | - | na[e] | - |
| Winter salt | Na or Cl | 0.2 (2) | - | 0.3 (3) | 0.3 (4) | 0.5 (6) | - | na[e] |

[a] Sum of two resolved secondary sulfate factors, see section 3.3 for details.

[b] Vehicular and industrial sources co-varied, see text for details.

[c] Vehicular factors include chemical characteristics of road dust (e.g. Ca, Mg).

[d] Sum of Ca and Al-Si enriched dust factors.

[e] Enrichment factor not calculated due to unresolved factor(s).

## Figure Captions

**Fig. 1.** Map of the five sampling sites in Iowa, with urban sites marked by stars and rural sits marked by circles.

**Fig. 2.** Annual average $PM_{2.5}$ concentrations at five locations in Iowa, with Cedar Rapids, Des Moines, and Davenport representing urban areas and Montgomery and Van Buren representing rural areas.

**Fig. 3.** Seasonal variations of secondary tracers ($NH_4^+$, $NO_3^-$, $SO_4^{2-}$ and OC), combustion tracers (EC), crustal tracers (Si, Ca, and Al) and anthropogenic tracers (Fe, Pb, Zn and Cu) at the sampling sites in Iowa.

**Fig. 4.** A representative set of PMF factors deduced from $PM_{2.5}$ speciation data from Cedar Rapids. The left axis shows the log-transformed $PM_{2.5}$ mass fraction of each species, whereas the right axis shows the percent of species attributed to that factor. The error bar shows the model uncertainty as one standard deviation.

**Fig. 5**. Contributions of PMF-derived factors to $PM_{2.5}$ at the Cedar Rapids site from April 2009 to December 2012.

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Figure 1.

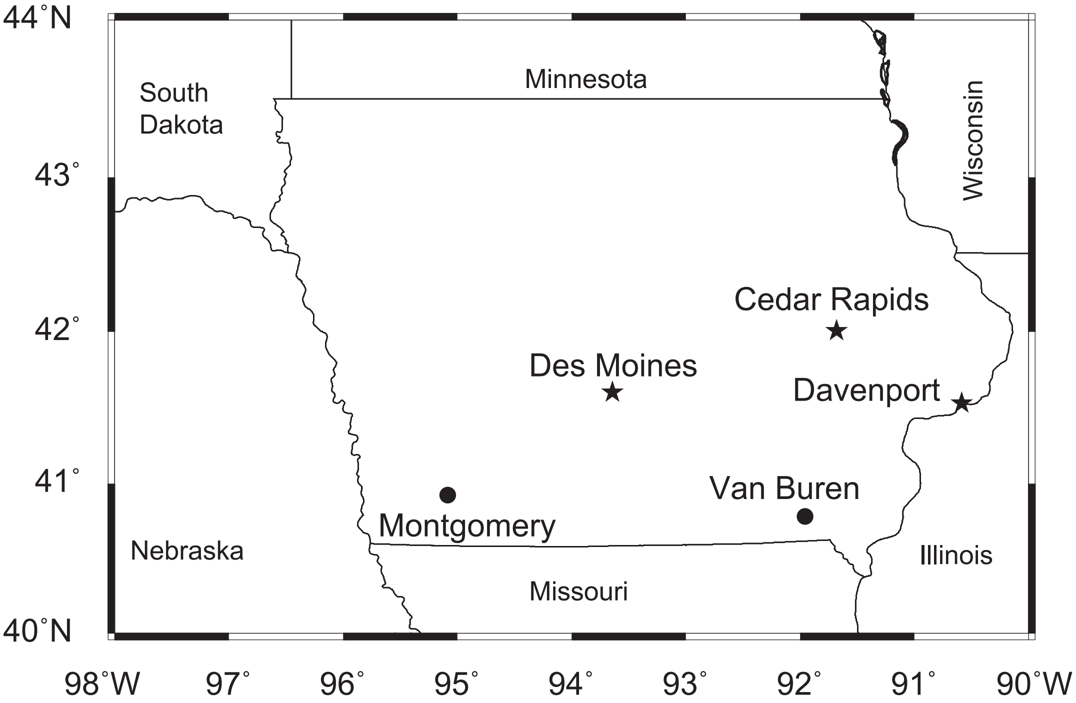

44˚N
43˚
42˚
41˚
40˚N
98˚W
97˚
96˚
95˚
94˚
93˚
92˚
91˚
90˚W
South Dakota
Minnesota
Wisconsin
Cedar Rapids
Des Moines
Davenport
Van Buren
Montgomery
Nebraska
Missouri
Illinois

Figure 2.

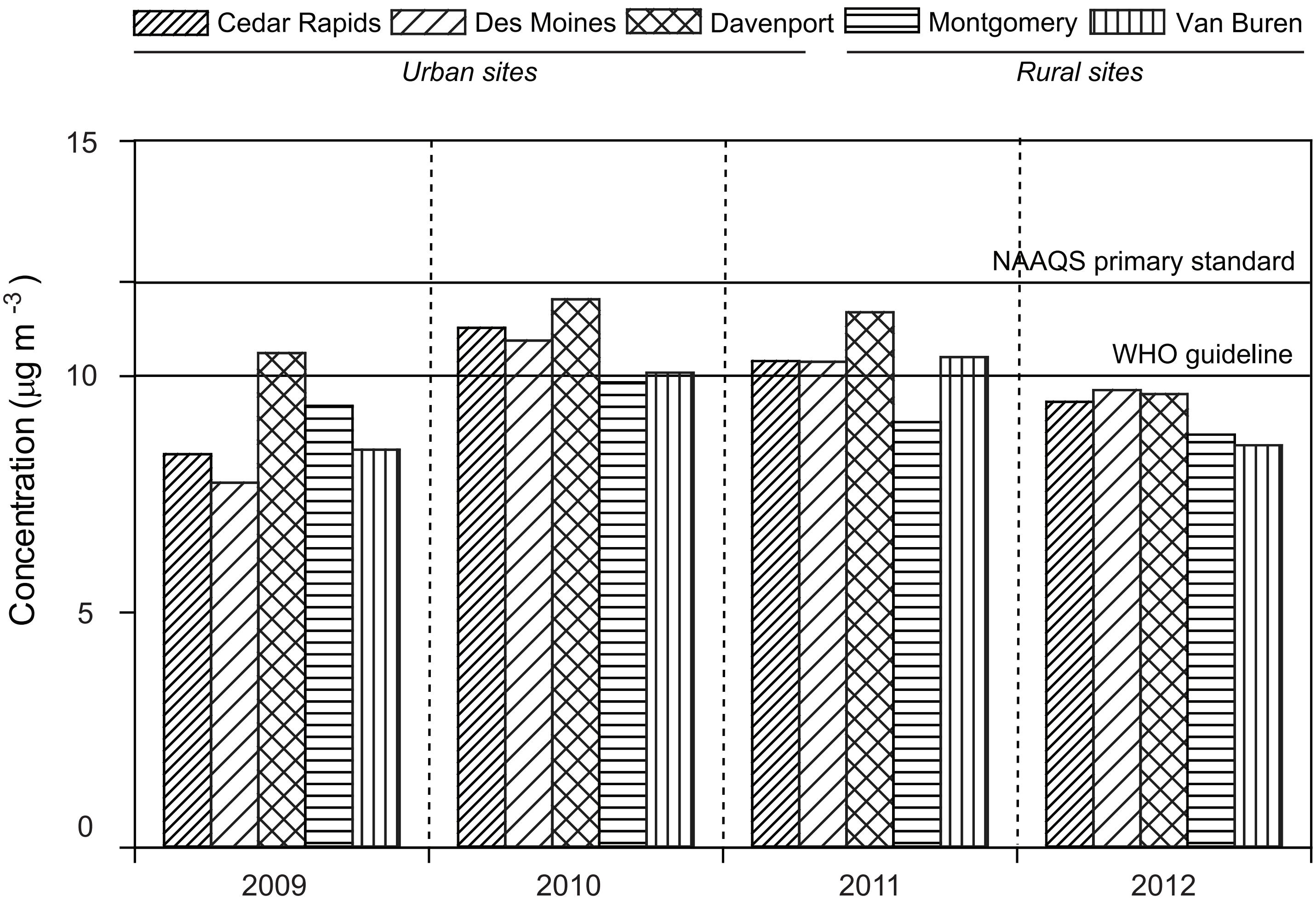

Cedar Rapids
Des Moines
Davenport
Montgomery
Van Buren
Urban sites
Rural sites
NAAQS primary standard
WHO guideline
Concentration (μg m -3 )
15
10
5
0
2009
2010
2011
2012

Figure 3.

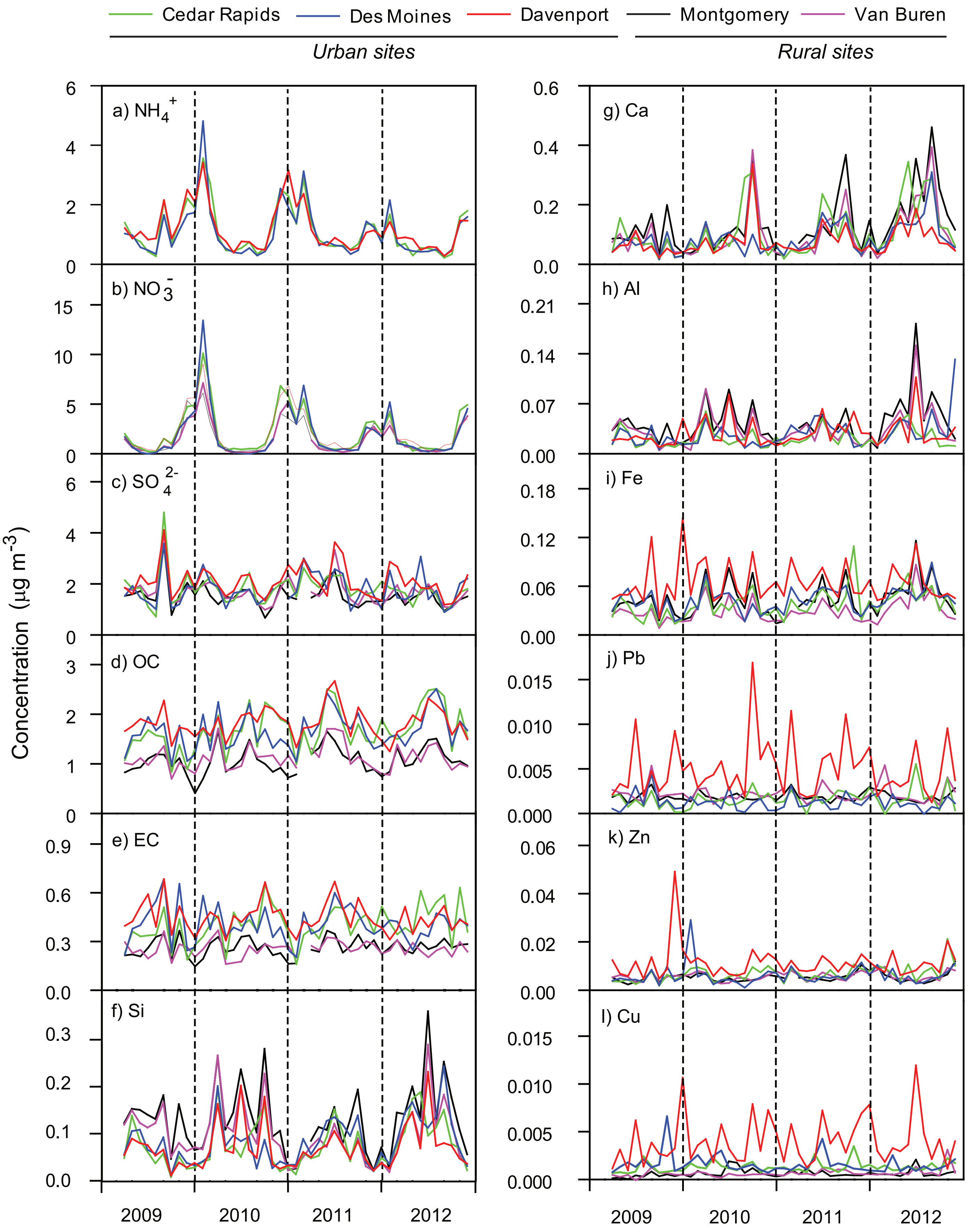

Cedar Rapids
Des Moines
Davenport
Montgomery
Van Buren
Urban sites
Rural sites
Concentration (µg m$^{-3}$)
a) NH$_4^+$
b) NO$_3^-$
c) SO$_4^{2-}$
d) OC
e) EC
f) Si
g) Ca
h) Al
i) Fe
j) Pb
k) Zn
l) Cu
0
2
4
6
5
10
15
1
3
0.0
0.3
0.6
0.9
0.1
0.2
0.4
0.07
0.14
0.21
0.00
0.06
0.12
0.18
0.000
0.005
0.010
0.015
0.02
0.04
2009
2010
2011
2012

Figure 4.

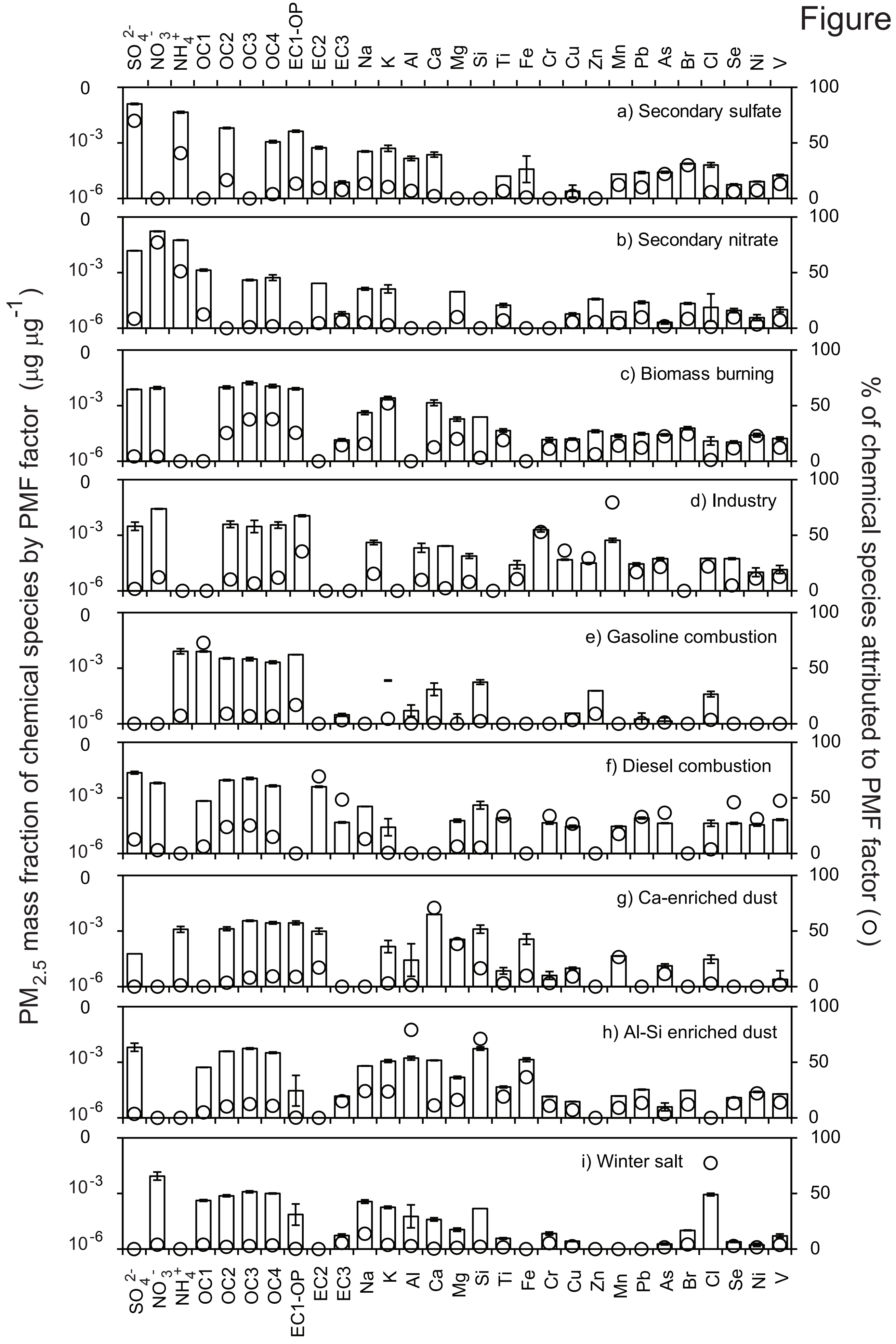
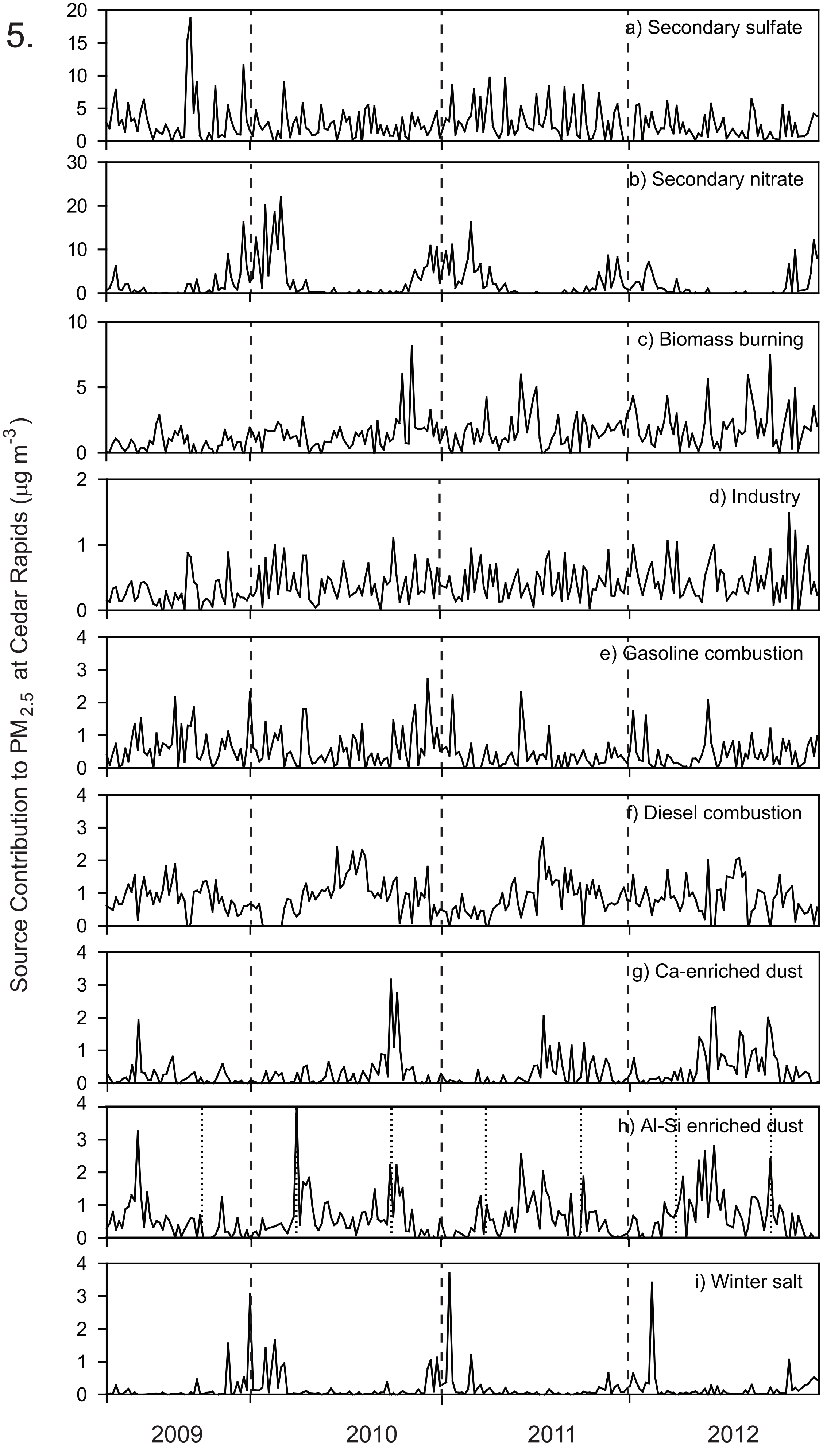

$SO_4^{2-}$
$NO_3^-$
$NH_4^+$
OC1
OC2
OC3
OC4
EC1-OP
EC2
EC3
Na
K
Al
Ca
Mg
Si
Ti
Fe
Cr
Cu
Zn
Mn
Pb
As
Br
Cl
Se
Ni
V
a) Secondary sulfate
b) Secondary nitrate
c) Biomass burning
d) Industry
e) Gasoline combustion
f) Diesel combustion
g) Ca-enriched dust
h) Al-Si enriched dust
i) Winter salt
0
$10^{-3}$
$10^{-6}$
100
50
0
$PM_{2.5}$ mass fraction of chemical species by PMF factor ($\mu g\ \mu g^{-1}$)
% of chemical species attributed to PMF factor (○)

Figure 5.


Source Contribution to $PM_{2.5}$ at Cedar Rapids ($\mu g\ m^{-3}$)
a) Secondary sulfate
0
5
10
15
20
b) Secondary nitrate
0
10
20
30
c) Biomass burning
0
5
10
d) Industry
0
1
2
e) Gasoline combustion
0
1
2
3
4
f) Diesel combustion
0
1
2
3
4
g) Ca-enriched dust
0
1
2
3
4
h) Al-Si enriched dust
0
1
2
3
4
i) Winter salt
0
1
2
3
4
2009
2010
2011
2012