Characteristics and Compositions of Airborne Fine Particulate Matter in Southwest Ohio, USA

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ABSTRACT

Southwest Ohio has been known for PM₂.₅ issues due to emissions from multiple local sources, such as industry and multimodal traffic, as well as regional impacts from sulfates, nitrates, and ammonia. To better understand the speciation characteristics of PM₂.₅ in this area, data from five monitoring sites, Taft, Hook Field, St. Bernard, Lower Price Hill, and Chase, were studied for the time period of 2003 to 2013. The total concentration of PM₂.₅ has decreased significantly since the last decade, from 13.41 µg m⁻³ in 2003 to 10.55 µg m⁻³ in 2013. The overall PM₂.₅ concentration also exhibited seasonal variations, with four out of five of the highest concentrations occurring in summer and the fifth one occurring in winter. Due to various air pollution control measures (such as the Cross-State Air Pollution Rule, and Mercury and Air Toxics Standards), both the total concentrations and the speciation of PM₂.₅ have changed over time. The most dominant components of PM₂.₅ include sulfates, organic matter (OM), and nitrates, which contributed 33.4%, 31.7%, and 17.7%, respectively (Taft data from 2009 to 2013). Elemental carbon (EC) and crustal materials, on the other hand, accounted for much smaller portions—2.84% and 3.61%, respectively. The highest concentrations of sulfate occurred in summer, while those for nitrates occurred in winter. EC and OM followed the same seasonal trends, peaking in fall and summer and dropping to their lowest levels in winter. Crustal materials exhibited the lowest concentrations in winter. A comparison of Cincinnati (the Taft site) with other major cities nearby reveals that the highest concentration of PM₂.₅ and the largest fraction of sulfates is found in Cincinnati. Efforts to control these emissions are still necessary.

Keywords: PM₂.₅; Chemical speciation; Southwest Ohio; Sulfate.

INTRODUCTION

It has been well demonstrated that airborne fine particulate matter (PM₂.₅), which refers to particulate matter of aerodynamic diameter less than 2.5 µm, is a significant contributor to visibility reduction (Islam et al., 2007; Sena et al., 2013). In addition, PM₂.₅ also contributes to detrimental effects on human health, such as pulmonary and chronic diseases for it can penetrate directly into the lung (Brunekreef et al., 2002; Contini et al., 2014; Li et al., 2015). As an example, Boldo et al. (2006) reported the effects of long-term exposure to PM₂.₅ in 23 European cities and it was estimated that 16,926 premature deaths from all causes, including 11,612 cardiopulmonary deaths and 1,901 lung cancer deaths, could be prevented annually if long-term exposure to PM₂.₅ levels were reduced to 12 µg m⁻³ in each city (Boldo et al., 2006).

PM₂.₅ is a complex mixture which includes sulfate, nitrate, elemental carbon, organic carbon, and elements such as metals and crustal materials, etc. Each component may have different emission characteristics and health impacts (Burnett et al., 2000; Ostro et al., 2007; Ianniello et al., 2011; Villalobos et al., 2015; Zhao et al., 2015). A number of sources such as power plants, refineries, chemical plants, road runoffs, fugitive dust, natural erosions and even cooking activity contribute to the ambient PM₂.₅ concentrations (McDonald et al., 2003; Bell et al., 2007). There are many studies on the PM₂.₅ speciation in various cities in the US, Europe and around the world, which will not be repeated here. However, as part of the American heartland, there have been less reports on the long-term PM₂.₅ speciation trends of the southwest Ohio area. Cincinnati is the largest metropolitan area in southwest Ohio on the Ohio River,
and is a hub of intermodal transport. It is the 14th largest port in the US (Army Corps of Engineers, 2015) and the 4th largest in the US in total rail mileage and highest in density of rail lines (ORDC, 2014). It has been known as a diesel hotspot due to high diesel traffic, and there has been a multiple year study, the Cincinnati Childhood Allergy and Air Pollution Study (CCAAPS), which found the increase correlation of children who lived near diesel traffic with asthma rate (Cheng et al., 2014).

The active manufacturing activities in the past resulted in still many industries in this area. Together with multimodal traffic, these all contribute to PM$_{2.5}$ emissions in this area. Selected areas in Cincinnati (e.g., Hamilton County) have been on the “most polluted city” list of the American Lung Association for many years. The complexity of emission sources, together with known air quality issues all warrant the necessity of this study.

The goal of this work is to study PM$_{2.5}$ speciation in southwest Ohio in the recent decade, to better understand emission characteristics, e.g., the seasonal trends of various species, and the compositional changes over time. Comprehensive information on the chemical composition of airborne PM$_{2.5}$ in Cincinnati can be useful to source apportionment, to propose emission abatement strategies and to estimate public health impacts.

**DATA AND ANALYTICAL APPROACH**

**Sampling Sites and Data Collected**

The PM$_{2.5}$ speciation data were obtained from the Chemical Speciation Network (CSN) of the US EPA, through the Air Quality System (AQS). The AQS is designed for data access by state and local agencies, consultants and other users.

The CSN was established in 2000, and consists of 189 sites as of 2014, out of which 53 sites will not be funded (Solomon et al., 2011; Landis et al., 2014). The goal of the CSN is to support effective PM$_{2.5}$ management, such as the state implementation plans, designation of non-attainment areas, formulation of control strategies, etc. The network data are also very helpful in model development, supporting health studies, and trends studies.

As shown in Fig. 1, speciation data from five CSN sites in southwest Ohio were evaluated. These sampling sites include Taft, Hook Field, St. Bernard, Lower Price Hill, and Chase. Taft (site A) is located right off exit 3 on I-71, which is close to the University of Cincinnati, several major hospitals, three miles south of a coal power plant, one mile southeast of a natural gas power plant and is also affected by various local sources. There are a mix of traffic, stationary and area PM sources (such as residential wood stoves). The pollution pattern is representative for an urban site in the Midwest US. St. Bernard (site B) is north of Cincinnati and near a railroad switch yard. Lower Price Hill (site C) is in an economically disadvantaged neighborhood close to the Ohio River. Chase (site D) is on the other side of the Ohio River in Kentucky, 5 miles south of the Taft site. Hook Field Airport (site E) is located in Middle town, OH, approximately 40 miles north of the Taft site. The land use type is commercial and its location type is suburban, which differs from Taft.
Both Hook Field and Chase have data only from 2001 to 2010, and both became inactive afterwards. St. Bernard and Lower Price Hill both have only two years of data, 2007 to 2008 and 2002 to 2003 respectively (Table 1). Taft is still active and represents a downtown scenario. Therefore, the data from the Taft site is the most important in this paper and data from this site will be used for representing Cincinnati, OH, for further analysis.

Speciation Sample Collection and Analysis

The CSN sites collect 24-hour filter based samples using chemical speciation samplers. The Spiral Ambient Speciation Sampler (SASS, Met One Instrument Inc., Grants Pass, Oregon, USA) is used to collect PM$_{2.5}$ speciation samples for all the sampling sites in this paper. The SASS sampler has five separate channels, which collects different fractions of the particulate matter. For example, one channel collects particulate matter on a Teflon filter that is analyzed for atmospheric concentrations of PM$_{2.5}$ mass and 48 trace elements. The denuder coated with MgO is used in another channel to remove acidic gases from the sampled air stream and a nylon filter is used for sulfate, nitrate and ammonium analysis. Meanwhile a carbon black honeycomb denuder in a third channel is used to remove semi-volatile organic compounds that may interfere with the OC measurement. A quartz filter collects total organic and elemental carbon (OC/EC). The fourth and fifth channels can be used for duplicates or control. The flow rate through each channel is nominally 6.7 L min$^{-1}$. The liquid water portion of the PM was not collected nor analyzed.

The mass of PM$_{2.5}$ is determined gravimetrically. Trace elements, such as different metals and crustal materials, are analyzed by X-ray fluorescence method. Thermal-optical reflectance method is used for determining OC and EC (Solomon, 2001; Chow et al., 2004). Water-soluble species, such as sulfate, nitrate and ammonium are quantified by ion chromatography (Solomon et al., 2001, 2014).

Data Analysis

The speciation data were reported every 6 days before Jan. 2011, and every 3 days after Jan. 2011. Data were aggregated into monthly averages, seasonal and annual averages, and averages in multiple years for comparison and analysis.

For the study of the seasonal trend, the three months with the highest average temperature was defined as summer. Similarly, the coldest three months was defined as winter (Pacas et al., 2011). In Cincinnati, OH, summer corresponds to June, July and August, while winter covers December, January (next year), and February (next year) (Pacas et al., 2011).

Geological materials are also referred to as crustal materials, which mainly consists of oxides of aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), iron (Fe) and other metal oxides. The crustal materials can contribute 50 percent of PM$_{10}$, but only 5 to 15 percent of PM$_{2.5}$ (Chow and Watson, 1992). The formula for the crustal materials is defined as follows (Rao et al., 2003):
Crustal = 2.2[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]  \hspace{1cm} (1)

OM (organic matter) accounts for other organic compounds bounded with the organic carbon (OC), such as H, O, N, S, etc. Organic carbon concentration is usually converted into organic matter concentration by multiplying the organic carbon concentration by a constant, K, which can range from 1.2 for freshly emitted PM in urban area to 2.6 for aged PM (Chow et al., 2015). Recent research shows that 1.6 for urban and 2.1 for nonurban aerosols are more appropriate (Arimoto et al., 1996). 1.6 is used in this study.

The LADCO (Lake Michigan Air Directors Consortium), suggested that the PM mass reconstruction in Cincinnati (OH) and other Lake Michigan states should use the following equation:

\[ \text{PM}_{2.5} = 1.375 \times \text{sulfate} + 1.29 \times \text{nitrates} + 1.6 \text{OC} + \text{other} \hspace{1cm} (2) \]

where the ammonium fraction is not used, and assumed the sulfate fraction as ammonium sulfate and the nitrate fraction as ammonium nitrate. This is one of the mass reconstruction methods (Chow et al., 2015) and has been used in many LADCO studies (Hand et al., 2011).

**RESULTS AND DISCUSSION**

**Ambient Concentrations**

Averaged ambient concentrations of PM$_{2.5}$ and their chemical components in five sampling sites are presented in Table 1. The Taft data from 2003 to 2010 were averaged to compare with those from Chase and Hook Field Airport. It is found that both the PM$_{2.5}$ concentrations and their chemical components are close. This may be partially due to their proximity (Li et al., 2015). In addition, since Taft has the most data, the rest of the analysis will mainly focus on the Taft site.

The average PM$_{2.5}$ concentration at Lower Price Hill (site C) is the highest among all five sites, with also much higher OM fractions (48% vs. 39% at Taft) and slightly higher sulfate fractions (46% vs. 42% at Taft) as well as slightly higher EC fractions than the Taft site. This is expected as the Lower Price Hill site is close to the downtown rail switch yard and also is subject to barge traffic on the Ohio River. Comparing with the Taft site (13.9 µg m$^{-3}$ during Aug. 2006 to July 2007, has no data Aug. 2007–July 2008), the St. Bernard site (sampling site B) is slightly higher in PM$_{2.5}$ concentrations, but with much higher EC (7% vs. 4%) and OM fractions (52% vs. 39%). The St. Bernard site was set on a roof of a private business next to the rail line and a bus yard across the street, which can be subject to higher diesel emissions from both diesel school buses and trains. Data from B and C sites suggested rail emissions should be monitored more in the future, not only due to the higher emissions but also due to the lack of data on this type of sources.

The annual PM$_{2.5}$ average is decreasing at Taft site from 2003 to 2013 (LADCO, 2003; Li et al., 2015), which is likely due to various control measures, especially sulfate source control (Blanchard and Tanenbaum, 2008). The Cross-State Air Pollution Rule requires 27 states in eastern US to improve PM$_{2.5}$ and ozone compliance by reducing SO$_2$ and NO$_x$. Mercury and Air Toxics Standards requires the electricity industry to install new control equipment and retire outdated facilities (Burtraw et al., 2012). In addition, the Clean Air Interstate Rules requires the reduction of NO$_x$ and SO$_2$ emissions from contributing to downwind states. For mobile sources, under US EPA's Midwest Clean Diesel Initiative, Ohio Clean Diesel School Bus Fund provide funds for school buses to install control equipment to reduce diesel emissions. The sulfur level in diesel fuel also decreased from 500 ppm to 15 ppm in 2007. This decreasing trend is also observed in other cities, such as St. Louis, MO (Lee and Hopke, 2006), and various sites in New York (NYDEC, 2015). Therefore, only the more recent data, e.g., from 2009 to 2013, is presented in this paper.

Fig. 2 shows the overall PM$_{2.5}$ data from 2009 to 2013 at Taft. The highest PM$_{2.5}$ concentration occurred in July 2011, with the monthly average concentration of up to 21.463 µg m$^{-3}$, approximately twice as high as the average PM$_{2.5}$ concentration (11.88 µg m$^{-3}$). The lowest PM$_{2.5}$ value occurred in October 2012 with a monthly average value of 6.35 g m$^{-3}$. Referencing the past five years, the annual concentration decreased by about 15 to 20 percent in 2012 and 2013, compared to those of 2009, 2010 and 2011. For the PM$_{2.5}$ chemical speciation, sulfate is the most dominant taking up to 33.43%, followed by organic matter (31.71%) and nitrate (17.71%). The combined secondary components, sulfate and nitrate, makes up about half (49.19%) of the PM$_{2.5}$ speciation. Fractions of EC and crustal materials did not change much over the years.

**Seasonal Variations of PM$_{2.5}$ Components**

Monthly speciation trends were calculated each year from 2009 to 2013 and presented in Fig. 3. The trends remained similar over the years. The fractions of sulfates and nitrates fluctuate with season, while those of other components
Fig. 3. PM$_{2.5}$ speciation monthly data, Taft 2009 to 2013, (a) 2009, (b) 2010, (c) 2011, (d) 2012, and (e) 2013. The X-axis represents the twelve months from January to December, dots represent averaged PM$_{2.5}$ concentration.

also demonstrated seasonal trends. Similar monthly trends were also reported by Martuzevicius et al. (2005).

Fig. 4 shows the seasonal trends in Taft from 2009 to 2013. In summer (Jun. through Aug.) and winter (Dec. through Feb.), the PM$_{2.5}$ concentration is always larger than those in the spring and fall. Four of the highest PM$_{2.5}$ concentrations occurred in the summer, while only one (in 2010) occurred in winter. Two (Apr. 13, Apr. 12) of the five lowest PM$_{2.5}$ monthly averages out of the 5-year study period occurred in the spring while three were in the fall (Oct. 12, Nov. 11, Nov. 13). Higher concentrations observed during the summer can be related to energy consumption (for air conditioning), increased secondary aerosol formation, and increased traffic, etc. (Wang et al., 2017).
Fig. 5 clearly shows the opposite seasonal trends of sulfates and nitrates at the Taft site. Sulfates reach the maximum in the summer and are the lowest in the winter, while nitrates peaks in the winter and are the lowest in the summer. The correlation between them is –0.29, which indicates a reversed trend of these two species, but not a very strong one. The major expectation of this trend is higher SO$_2$ conversion in the summer and higher volatility of NH$_4$NO$_3$ in the warm period, while lower temperatures (in winter) favor nitrate condensation. The combination of these factors might account for the higher sulfate production and the volatilization of nitrate species in summer. Furthermore, the higher winter NO$_x$ levels may also account for the higher nitrate formation in the cold season (Arimoto et al., 1996).

A few studies used the annual average nitrates to sulfates ratio to evaluate relative contributions between mobile and stationary sources. A high ratio (2–5) shows dominant impacts from traffic source, while a low ratio (0.3–0.5) suggests more impacts from stationary sources (Arimoto et al., 1996; Yao et al., 2002). Table 2 shows the annual averages of nitrates to sulfates ratio at Taft site, which presented an increasing trend, especially in recent years. The average is 0.53 during the 2009 to 2013 period, which increased from 0.39 during the 2003 to 2008 period (Li, 2015). This corresponds to stationary sources reduction by various control measures, such as the Cross-State Air Pollution Rule (CSAPR) and Mercury and Air Toxics Standards (MATS) (Burtraw et al., 2012; US EPA, 2015; Davis et al., 2016). Meanwhile, traffic emissions have been increasing in recent years (Shahiduzzaman, 2017), which may require further study and control.

Seasonal EC/OM ratios were also studied from 2009 to 2013, which is shown in Fig. 6. The ratios of annual average
Table 2. Nitrate/Sulfate ratio in Taft from 2003 to 2013.

<table>
<thead>
<tr>
<th>Year</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$/SO$_4^{2-}$</td>
<td>0.40</td>
<td>0.44</td>
<td>0.34</td>
<td>0.40</td>
<td>0.40</td>
<td>0.36</td>
<td>0.48</td>
<td>0.58</td>
<td>0.46</td>
<td>0.52</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Fig. 6. OM and EC seasonal trend, Taft, 2009 to 2013 (Sp: Spring, Su: Summer, F: Fall, W: Winter).

mostly ranged from 0.086 to 0.096 with a correlation coefficient of 0.72. Higher EC/OM ratios (0.11) mostly occurred in the fall and summer. Similar trends have also been reported in a Cincinnati study earlier (Grinshpun et al., 2014), which may be due to the contribution of heavy-duty diesel traffic. Periods of higher OM in the summer may indicate a photochemical contribution (Peter et al., 2004).

Fig. 7 shows seasonal variations of crustal materials, which represent from 1.57% to 6.62% of the total PM$_{2.5}$. The lowest concentrations are always observed in the winter, higher concentrations during spring, summer and fall are likely related to the growing/harvesting activities.

Comparison of Cincinnati, OH, with Other nearby Cities

PM$_{2.5}$ speciation data from “nearby” CSN sites that are subject to the same air mass or have similar industrial settings were also compared. These sites include Chicago, IL; St. Louis, MO; and Pittsburgh, PA, and data used are from 2011 to 2013 (Table 3).

Fig. 8 shows the fractions of PM$_{2.5}$ speciation and the relative locations of these sites. While the fraction of sulfates is the largest in Cincinnati, OM becomes the largest fraction for the other 3 cities.

As shown in Table 3 and Fig. 8, during this period, Chicago has the highest annual average PM$_{2.5}$ concentration (14.2 µg m$^{-3}$) while other three cities are all within the 12 µg m$^{-3}$ standard. The combined fractions of sulfates and nitrates reaches almost half in the other three sites except Chicago (39%), suggesting that Cincinnati, St. Louis and Pittsburgh may be impacted by stationary and secondary aerosols more than Chicago.

The much higher nitrates to sulfates ratio in Chicago indicates a stronger mobile source impact than the other cities, and is likely more diesel traffic (indicated by EC/OM ratio).

CONCLUSIONS

PM$_{2.5}$ compositions in southwest Ohio were analyzed using data from the Chemical Speciation Network of US EPA, especially the data from the Taft site located in Cincinnati, OH. The average annual PM$_{2.5}$ decreased by 23% between 2003 and 2013 and has been within the 12 µg m$^{-3}$ limit since 2012. This reduction may be due to various regulations and control technologies that have been implemented on stationary and mobile sources. Based on data from 2009 to 2013, the PM$_{2.5}$ in Cincinnati is composed of sulfate (3.97 µg m$^{-3}$), nitrate (2.10 µg m$^{-3}$), OM (3.77 µg m$^{-3}$), EC (0.34 µg m$^{-3}$), and crustal material (0.43 µg m$^{-3}$). The most dominant component is still sulfate, although both its quantity and relative fraction have decreased steadily compared with the 2003–2008 period. The gravimetric PM$_{2.5}$ concentration also exhibited a seasonal trend: Four out of the five highest concentrations occurred in summer and one occurred in winter, with lower levels in spring and fall. Seasonal variations can likewise be found in the different PM$_{2.5}$ components, e.g., the concentration of sulfate is always highest in the summer and lowest in the winter, whereas nitrate is lowest in the summer and highest in the winter. Crustal materials, on the other hand, display the lowest concentrations in winter. A comparison with nearby cities reveals similar trends, with the exception of Chicago. Continued efforts to further reduce stationary-source emission in the Cincinnati region are necessary in order to decrease the fractions of sulfates and nitrate in PM$_{2.5}$. \[\text{Fig. 7 shows seasonal variations of crustal materials, which represent from 1.57\% to 6.62\% of the total PM}_{2.5}. \]
Fig. 7. Seasonal trend of the crustal material, Taft, 2009 to 2013.

Table 3. CSN sites and select parameters (2010–2013) (µg m⁻³).

<table>
<thead>
<tr>
<th>Location</th>
<th>Cincinnati OH</th>
<th>Chicago IL</th>
<th>St Louis, MO</th>
<th>Pittsburgh, PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site ID</td>
<td>39-061-0040</td>
<td>17-031-0057</td>
<td>29-510-0085</td>
<td>42-003-0008</td>
</tr>
<tr>
<td>Averaged PM₂.₅ concentration</td>
<td>11.3</td>
<td>14.2</td>
<td>11.19</td>
<td>10.23</td>
</tr>
<tr>
<td>Fractions of sulfates and nitrates combined</td>
<td>0.49</td>
<td>0.39</td>
<td>0.45</td>
<td>0.48</td>
</tr>
<tr>
<td>Nitrates to sulfates ratio</td>
<td>0.53</td>
<td>1.00</td>
<td>0.68</td>
<td>0.43</td>
</tr>
<tr>
<td>EC/OM ratio</td>
<td>0.09</td>
<td>0.12</td>
<td>0.11</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Fig. 8. Comparison of PM₂.₅ composition from nearby cities, 2011 to 2013 (µg m⁻³).
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