Conceptual Models of $PM_{2.5}$ in Great Lakes Region

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1. Background

Atmospheric particulate matter (PM) is an air pollutant containing both solid particulates and liquid droplets. Based on sizes, PM with diameter less than 2.5 micrometers is named $PM_{2.5}$ and is frequently referred to as “fine particulates”. Fine particulates pose a greater risk to human health and environment than do larger particulates. As $PM_{2.5}$ is extremely small, it can enter lungs and bloodstreams easily, which could cause some potential heart, lung and respiratory symptoms and diseases such as asthma and heart attacks. Its chemical composition is complicated, including nitrate, sulfate, ammonium, soil, elemental carbon and organic carbon. Moreover, since it is capable of being transported over long distance, $PM_{2.5}$ is also related to environmental problems and can affect ecosystems. Therefore, $PM_{2.5}$ is regulated by the U.S. Environmental Protection Agency (U.S. EPA) under National Ambient Air Quality Standards (NAAQS) as one of six criteria air pollutants (U.S. EPA, 2023).

1.1 $PM_{2.5}$ trends and concentrations in Great Lakes region

Figure 1 gives an overview of trends of 24-hour and annual $PM_{2.5}$ design values in Great Lakes region from 2001 to 2021. Starting from 2004, the median 24-hour design value was at or lower than NAAQS standard. From 2011 on, all design values in the region were lower than the level of the NAAQS. 24-hour design values continued to decrease until 2018 when the values began to increase again. Annual design value data showed a similar pattern. From 2009 onward, the median design value was at or lower than NAAQS standard. All design values were at or lower than the level of the NAAQS beginning in 2016. However, the annual design values became stable in 2018-2020 and then increased.

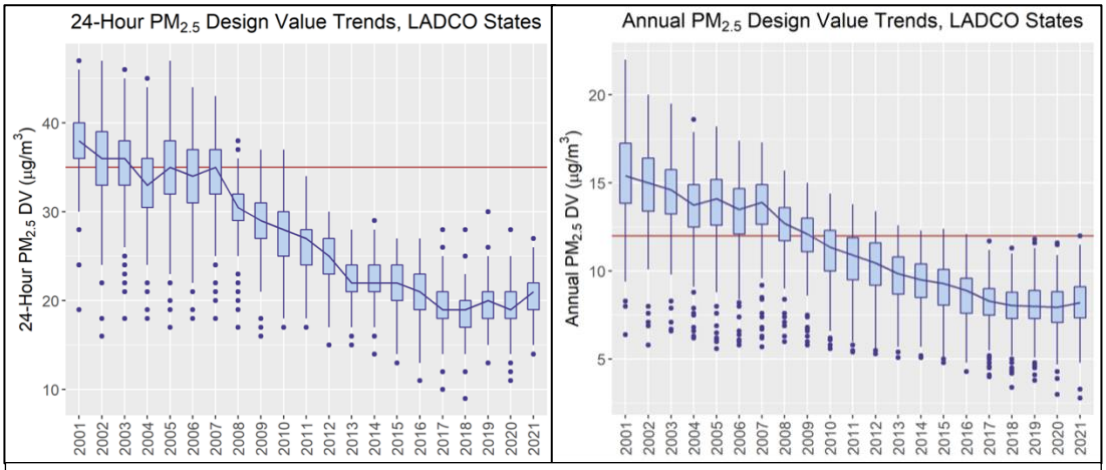

Figure 1. 24-hour and annual $PM_{2.5}$ design value trends in LADCO states (MN/WI/MI/IL/IN/OH) from 2001 to 2021. Box plots were applied in each year in which the middle line is the median value, the box encloses the middle half of values, and the whiskers and points show the range of other values, and the line connected the median value in each year. The red lines represent NAAQS standards. From LADCO $PM_{2.5}$ trends through 2021 slides.

In general, $PM_{2.5}$ concentrations decreased significantly over these 20 years, becoming much lower than the 24-hour NAAQS standard and slightly lower than the annual NAAQS. However, there is a trend in recent years that the concentration started to increase again, even though the values were still not exceeding the standards. Looking forward, U.S. EPA has proposed to lower the level of the annual $PM_{2.5}$ NAAQS to between 9.0 to 10.0 $\mu g/m^3$ and is taking comments on lowering the 24-hour NAAQS to as low as 25 $\mu g/m^3$ (U.S. EPA, 2023). If U.S. EPA finalizes these actions, many areas in the Great Lakes states could be out of attainment with the new NAAQS, as shown in Figure 1.

1.2 Drivers of $PM_{2.5}$ formation and accumulation

$PM_{2.5}$ is formed via two broadly different pathways. A small portion is directly emitted from sources, primarily from combustion of fuels in the industrial processes and vehicles (Hughes et al, 2021). Most $PM_{2.5}$ is produced by complex chemical reactions in the atmosphere from other air pollutants including sulfur dioxide (SO_2) and nitrogen oxides (NO_X) (U.S.EPA, 2023). In this way, since the formation and composition of $PM_{2.5}$ is complicated, with a series of chemical reactions and involvement of other pollutants, it is important to understand its speciation, which can provide some ideas about the best approaches to reduce $PM_{2.5}$ concentrations. Moreover, $PM_{2.5}$ can be carried over long distances, so understanding its physical transport is also critical in the understanding of $PM_{2.5}$. Additionally, both chemical reactions and physical transport are affected by meteorology such as temperature, wind speed, and wind direction. The study of meteorological conditions leading to high levels of $PM_{2.5}$ is therefore also a crucial topic in the study of $PM_{2.5}$.

1.2.1 Chemical composition and transformation

Some components in $PM_{2.5}$ such as soils, ammonium, elemental carbon (EC) and primary organic carbon (OC), come from primary sources. Ammonium (NH_3) is emitted from soils and livestock (Haste et al., 1998). In addition to primary sources, $PM_{2.5}$ produced via chemical reactions is defined as secondary aerosol, including secondary organic aerosol (SOA) and secondary inorganic aerosol, including nitrate and sulfate (Hughes et al, 2021). Specifically, SOA, as a secondary OC, is formed by a series of processes starting with anthropogenic and biogenic volatile organic compounds (VOCs) and including cloud processing and oxidation of gases derived from VOC oxidation. NOx and SO_2 are also able to enhance the formation of SOA from VOCs (U.S. EPA, 2019).

Among inorganic aerosol, nitrate and sulfate are also very important components of $PM_{2.5}$, and understanding their dynamics is important in the establishment of a useful conceptual model. The formation of nitrate is different during the daytime and nighttime. With the sunlight, OH reacts with NO_2 to form HNO_3, followed by the

partitions between gas and nitrate, while at night, in the absence of sunlight and NO, NO_3 is created by NO_2 and O_3 and then converted to N_2O_5 which is a source of the formation of nitrate (Stanier et al, 2012). Hence, nitrate can be synthesized continuously during the whole day in various chemical reactions and through these pathways, it becomes a major component in $PM_{2.5}$. For sulfate, it is mainly produced by oxidation of SO_2. In gas phase, SO_2 is oxidized by OH to form sulfate, and in fog drops, it can be oxidized by O_3, O_2 with catalysts or H_2O_2 (Pun & Seigneur, 1999).

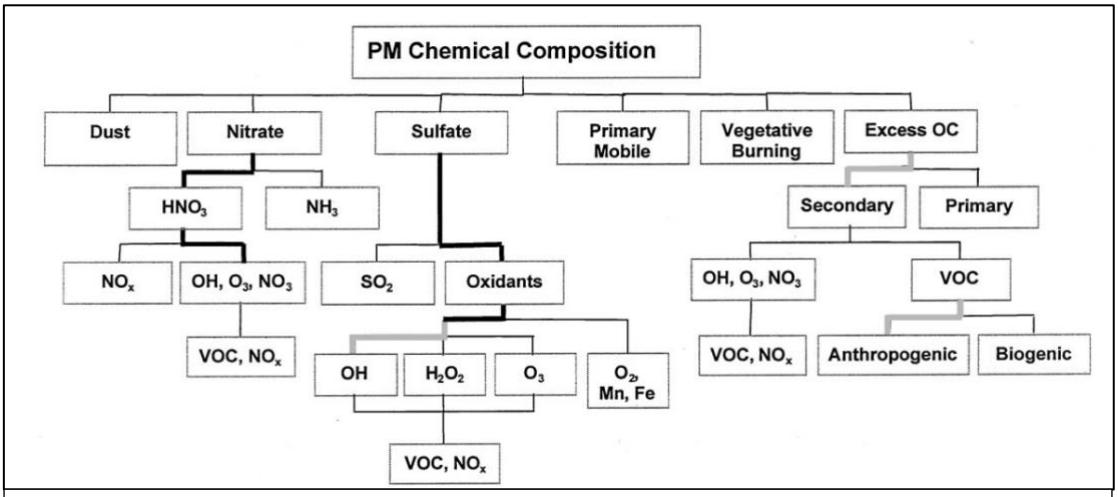

Figure 2. Breakdown of PM Chemical Composition. Bold lines represent the formation of secondary PM. From Pun and Seigneur, 1999.

1.2.2 Physical transport

$PM_{2.5}$ can be physically transported around the atmosphere via processes including horizontal advection, vertical mixing, wet deposition, and dry deposition. Pollutants can be carried over long distance aloft by horizontal advection where wind speed is always higher; then vertical mixing makes pollutants come back to the surface layer and mix with the air near ground. In these processes, wet and dry deposition change the budgets of some components (Pun & Seigneur, 1999). Such physical transport is heavily dependent on winds, making the study of wind speed and wind direction important.

2. Data and Methodology

This conceptual model is constructed based on data from the Air Quality System (AQS), a repository of ambient air quality data developed by EPA. To research $PM_{2.5}$ conditions in each state in Great Lakes region individually and compare them to figure out patterns, seven cities are picked, which are Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. Data from two periods, 2000-2004 and

2018-2022, are focused for finding variations over years, and we studied two seasons: summer and winter. As shown in Figure 3, $PM_{2.5}$ concentrations generally peaked in July and August in summer and December, January and February in winter, which were picked as the two seasons with high concentrations for the analysis of chemical speciation.

There are two components to our methodology: (1) an analysis of chemical speciation and (2) an analysis of meteorology including wind direction, wind speed, relative humidity and temperature. We studied six chemical components, which are nitrate, sulfate, ammonium, soil, organic carbon (OC) and elemental carbon (EC). However, only data for sulfate, nitrate and ammonium were available in 2000-2004.

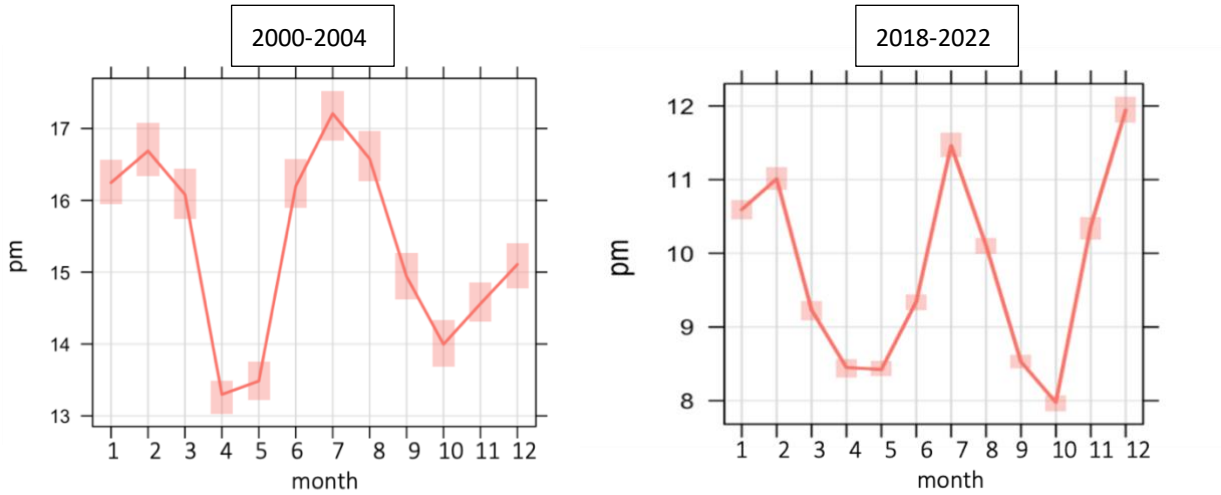

Figure 3. Monthly variations of PM2.5 concentrations in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis in (left) 2000-2004 and (right) 2018-2022. The red boxes represent 95% confidence intervals in the mean.

In the analysis of meteorology, we only focused on the period of 2018-2022 since many data were missing in the period of 2000-2004. To find the relationships between $PM_{2.5}$ concentrations and meteorological factors, including temperature, wind speed and relative humidity, the data were divided into three groups: high concentration, medium concentration and low concentration. Days with $PM_{2.5}$ concentration larger than 35 $\mu g/m^3$ were classified as high concentration, and the low concentration group included days with $PM_{2.5}$ concentration lower than 25 $\mu g/m^3$. Other days were in the medium concentration group. We focused on seasonal changes in meteorology as well by analyzing data in each season separately. As for wind direction, pollution rose plots were applied to explore the relationships.

3. Conceptual Model

A conceptual model is used to combine physical and chemical processes that affect $PM_{2.5}$ concentrations based on the quantitative data in a way that allows some patterns and processes to be characterized (Pun & Seigneur, 1999). In this work,

the conceptual model focused on chemical speciation and meteorology in summer and winter in 2000-2004 and 2018-2022.

3.1 $PM_{2.5}$ chemical speciation

3.1.1 The study of 2018-2022

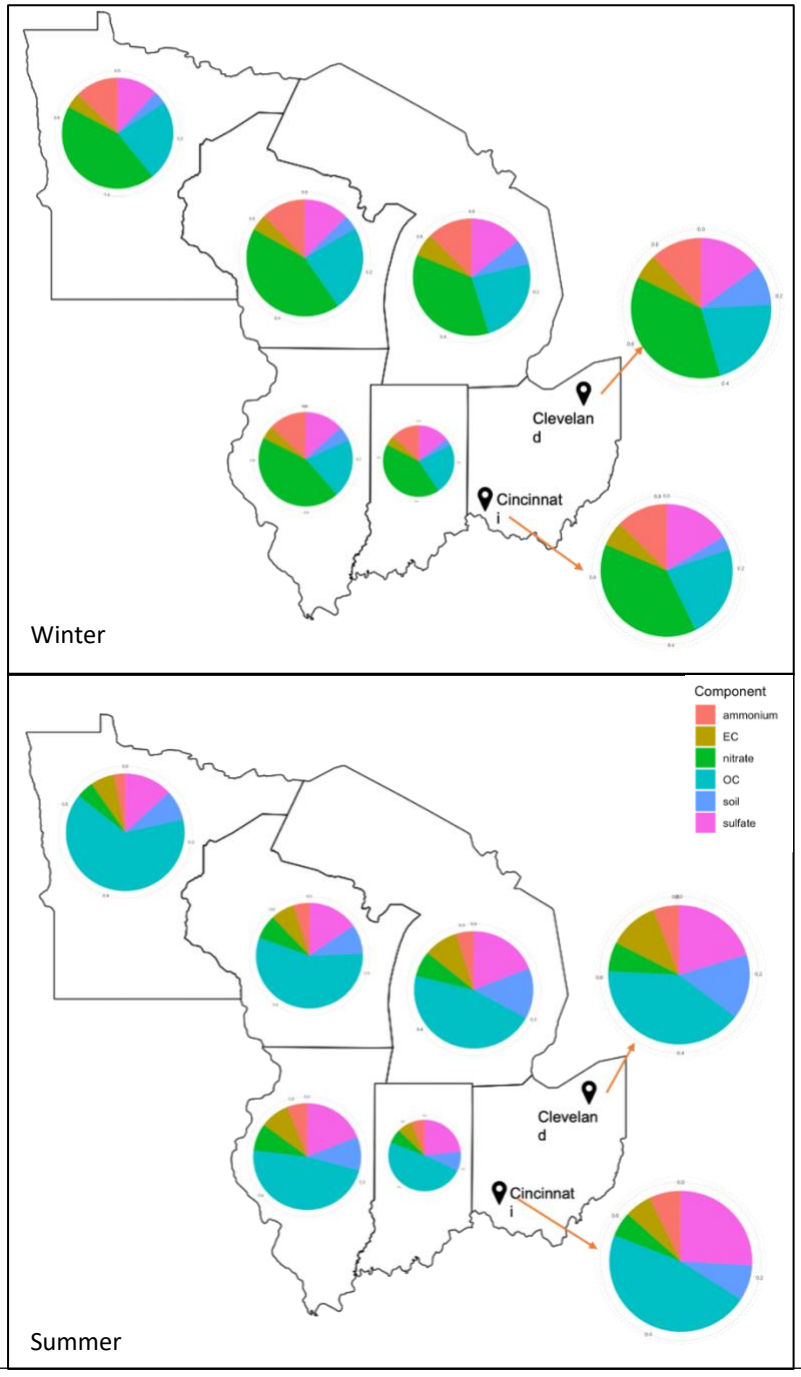

Figure 4. Pie charts of $PM_{2.5}$ chemical speciation in (down) summer (July and August) and (up) winter (December, January, February) in 2018-2022 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The colors stand for the six major components of PM2.5, which are sulfate, nitrate, ammonium, soil, EC and OC.

Since the formation of $PM_{2.5}$ is affected by chemical reactions which are different in summer and winter, there are clear seasonal patterns of chemical speciation showing in all seven cities. Generally, according to Figure 4, the proportions of concentrations of six components follow the order: OC >> sulfate > soil > nitrate ≈ EC > ammonium in summer, indicating OC is dominant in $PM_{2.5}$ in summer. The winter pattern in the proportion of concentrations is: nitrate > OC > ammonium ≈ sulfate > soil ≈ EC.

Parameter	Milwaukee	Mayville
$PM_{2.5}$ ($\mu g\,m^{-3}$)	17.1	11.7
Total nitrate ($\mu g\,m^{-3}$)	5.6	4.8
Total ammonia ($\mu g\,m^{-3}$)	3.3	3.3
Gas ammonia (ppb)	2.3	2.4
Nitrate aerosol/total nitrate	78 %	69 %
NO_y (ppb)	27	6.3
Temperature (°C)	−3	−5
Ozone (ppb)	22	31
OC ($\mu g\,m^{-3}$)	3.6	3.2
EC ($\mu g\,m^{-3}$)	0.52	0.3
Gas Ratio (d'less)	1.5	1.7

Table 1. Key mean measured values during the period 1 January–31 March 2009. From Stanier et al., 2012.

The result that nitrate is the dominant component in winter matches the winter nitrate study by Stanier et al. in 2009 in Milwaukee Mayville. As shown in Table 1, they found the concentration of nitrate was highest in $PM_{2.5}$ concentrations, compared with ammonia, OC and EC. In addition, they got that the large proportion of nitrate in winter was nitrate aerosol, which took roughly 80% (Stanier et al., 2012). In addition, in Table 1, the concentrations of OC and ammonium were relatively high as well, which were 3.6 and 3.3 μg/m^3 in Milwaukee respectively. This result also illustrates the winter

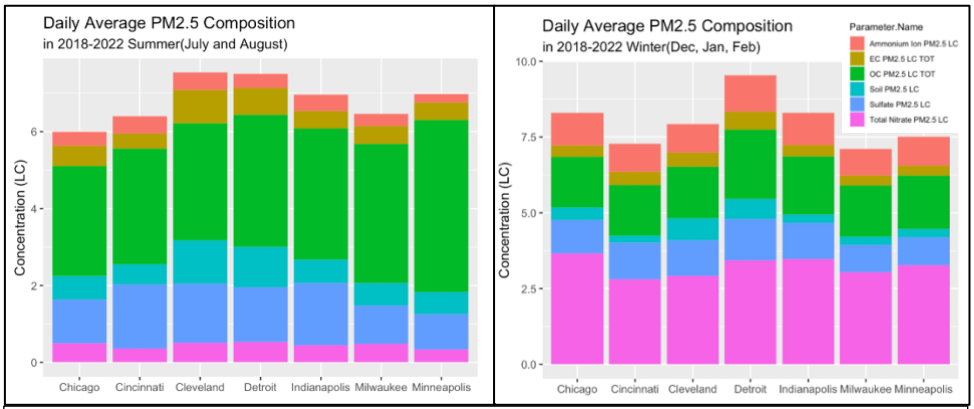

Figure 5. Bar plots of $PM_{2.5}$ chemical speciation in (left) summer (July and August) and (right) winter (December, January, February) in 2018-2022 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The colors stand for six major components of PM2.5, which are sulfate, nitrate, ammonium, soil, EC and OC.

pattern we found that the proportion of concentration is: nitrate > OC > ammonium.

In addition to the seasonal changes, some geographic differences also exist. As shown in pie charts in Figure 4, in summer, OC, the dominant component, contributed more than 60% to $PM_{2.5}$ concentration in Minneapolis, which was the highest proportion among six states, but only around 40% in Cleveland. In general, OC contributed more in the northern states (WI/MI/MN) than in the southern states in the summer. However, sulfate, as the second dominant component in summer, followed the opposite pattern. Based Figure 4 and 5, the proportion and concentration of sulfate were highest in Cincinnati and generally higher in southern states (OH/IN). In contrast to the regional patterns in PM2.5 composition in the summer, chemical composition was relatively uniform around the region in the winter.

3.1.2 The study of 2000-2004

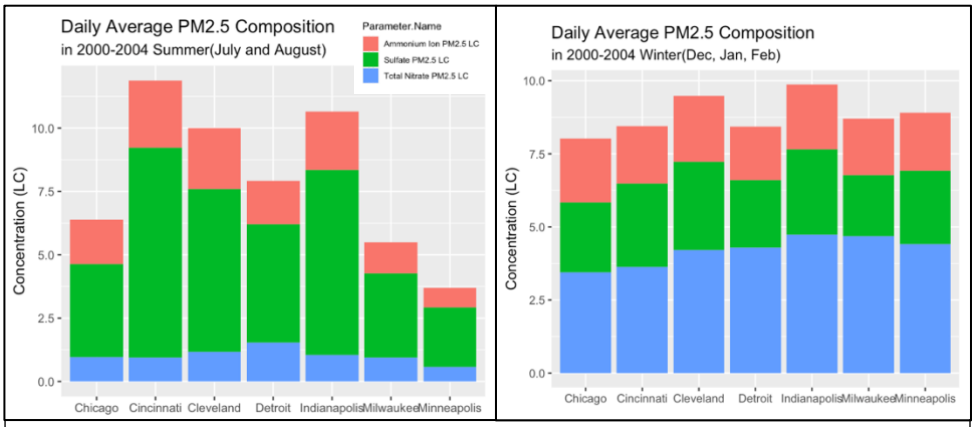

Figure 6. Bar plots of $PM_{2.5}$ chemical speciation in (left) summer (July and August) and (right) winter (December, January, February) in 2000-2004 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The colors stand for three major components of $PM_{2.5}$, which are sulfate, nitrate, and ammonium.

As indicated in Figure 6, in summer, $PM_{2.5}$ concentrations were much higher in southern states than in the north, more than 3 times as much in Cincinnati as in Minneapolis. And sulfate and ammonium were the biggest causes of this difference. In winter, there is no big difference of total $PM_{2.5}$ concentrations among these cities and $PM_{2.5}$ concentrations were highest in Indianapolis and lowest in Chicago.

Among the three components with available data in 2000-2004, as shown in Figure 7, sulfate was dominant in summer, followed by ammonium and nitrate. The proportion of sulfate was highest in Indianapolis and Cincinnati. In the winter, nitrate was still the dominant component, and its proportion was highest in Milwaukee. The proportion of sulfate was generally larger than that of ammonium in the winter.

Geographic pattern also showed up in Figure 6 and 7. In summer, sulfate contributed more than 60% to $PM_{2.5}$ concentration in eastern states (IN/OH/MI). Also in winter,

nitrate contributed more than half among these three components in northern states (WI/MN/MI) and generally less than half in the southern states. Moreover, the sulfate concentration was still higher in southern states than in the north.

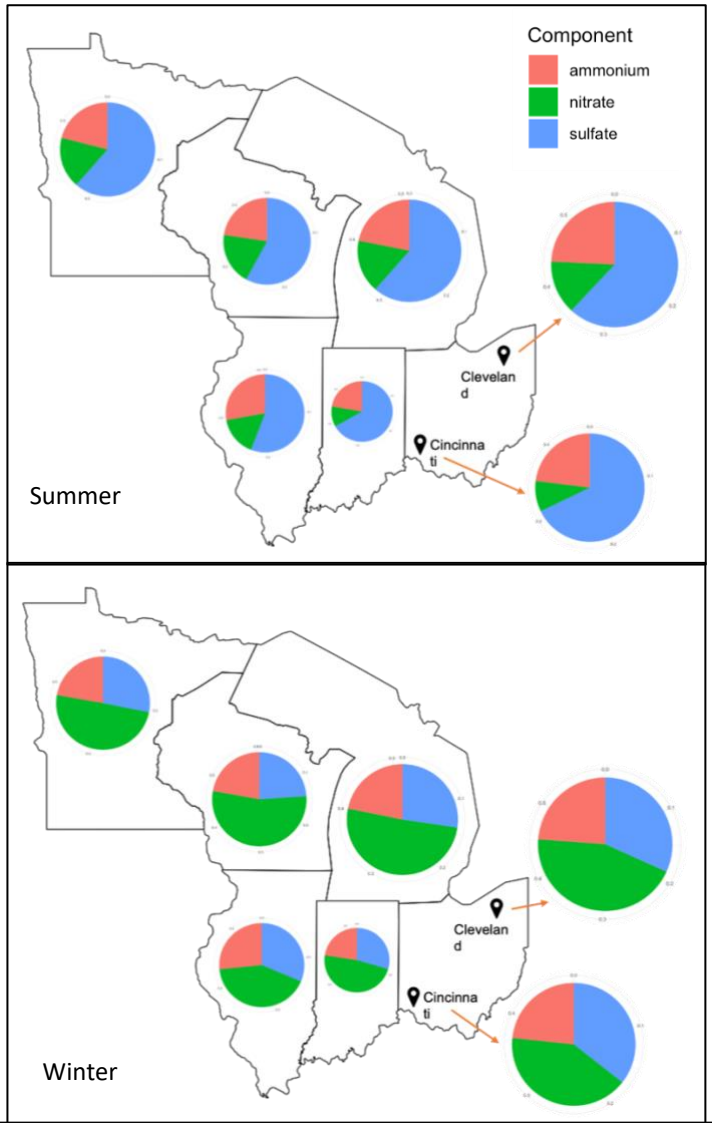

Figure 7. Pie charts of $PM_{2.5}$ chemical speciation in (up) summer (July and August) and (down) winter (December, January, February) in 2000-2004 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The colors stand for three major components of $PM_{2.5}$, which are sulfate, nitrate and ammonium.

3.1.3 Comparison of two periods

By comparing $PM_{2.5}$ speciation in these two periods, we can see how PM2.5 concentrations and composition has changed over time, as shown in Figure 8. Since there were only data of nitrate, sulfate and ammonium in 2000-2004, we only compared these three components. First, in winter, concentrations of these three components decreased by roughly a third from 2000-2004 to 2018-2022. The concentration of nitrate decreased by a fairly small amount, but the concentration of sulfate and ammonium decreased dramatically. Also, the relative proportion of sulfate and ammonium were similar in both periods, but the proportion of nitrate increased.

The cities with highest concentrations changed from Cleveland and Indianapolis to Chicago and Detroit, moving from south to north.

In summer, total concentrations of three components decreased much more than those in winter, with the largest decreases from sulfate. This change can be explained by the huge reductions in sulfur dioxide emissions from coal-fired power plants, especially those in the Ohio River Valley (U.S.EPA, 2023). The concentration of sulfate became more similar between the six states, and the concentrations of nitrate and ammonium became also became similar between the states and closer in magnitude to each other. The cities with highest concentration were still Cincinnati and Indianapolis, as well as Cleveland. The northern cities had the lowest totals.

Figure 8. Bar plots of $PM_{2.5}$ Speciation in summer and winter in 2000-2004 and 2018-2022. The colors stands for nitrate, sulfate and ammonium.

3.2 Meteorology

In AQS database, four meteorological variables were monitored and recorded, which were wind speed, temperature, relative humidity and wind direction. The same method was applied to the analysis of wind speed, temperature and relative humidity, which involved examination of properties on days classified into high, medium and low

concentration groups. We used pollution rose plots to study wind directions with different $PM_{2.5}$ concentrations.

Figure 9. The relationship between $PM_{2.5}$ concentration and meteorological variables (wind speed/relative humidity/temperature) in 2018-2022 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The colors of bars represent $PM_{2.5}$ concentration groups. Low con was set as $PM_{2.5}$ concentration lower than 25 ug/cm^3. High con was set as $PM_{2.5}$ concentration larger than 35 ug/cm^3. And med con was between low and high con.

3.2.1 Wind speed, temperature and relative humidity

Figure 9 includes the relationships between $PM_{2.5}$ concentrations and three meteorological variables, wind speed, temperature and relative humidity in these seven cities. However, because $PM_{2.5}$ concentration and meteorological data were not both recorded in some days in 2018-2022, some columns of medium and high concentrations were missing.

General patterns for each variable were clear: (1) The higher wind speed is, the lower $PM_{2.5}$ concentration is in all seasons, and wind speed was lower in summer than in winter. (2) In summer, the higher temperature is, the higher $PM_{2.5}$ concentration is. As for relative humidity, the patterns were opposite in winter and summer: In summer, the lower relative humidity is, the higher concentration is, while in winter, the higher relative humidity is, the higher concentration is. In addition, low wind speed and relatively warm temperatures tend are conducive to PM2.5 formation in both summer and winter. Whereas high relative humidity appears to enhance PM2.5 formation in the winter but not in the summer.

However, there were some exceptions to these findings even though data in most cities follow the patterns. For example, in wind speed plot in Figure 9, wind speed was highest in the days with high concentration in Indianapolis in winter, which was opposite to our general pattern. This may result from the limited data size, or this could result if there were large emissions on the days with high concentration or if the wind blew from large sources on those days.

3.2.2 Wind direction

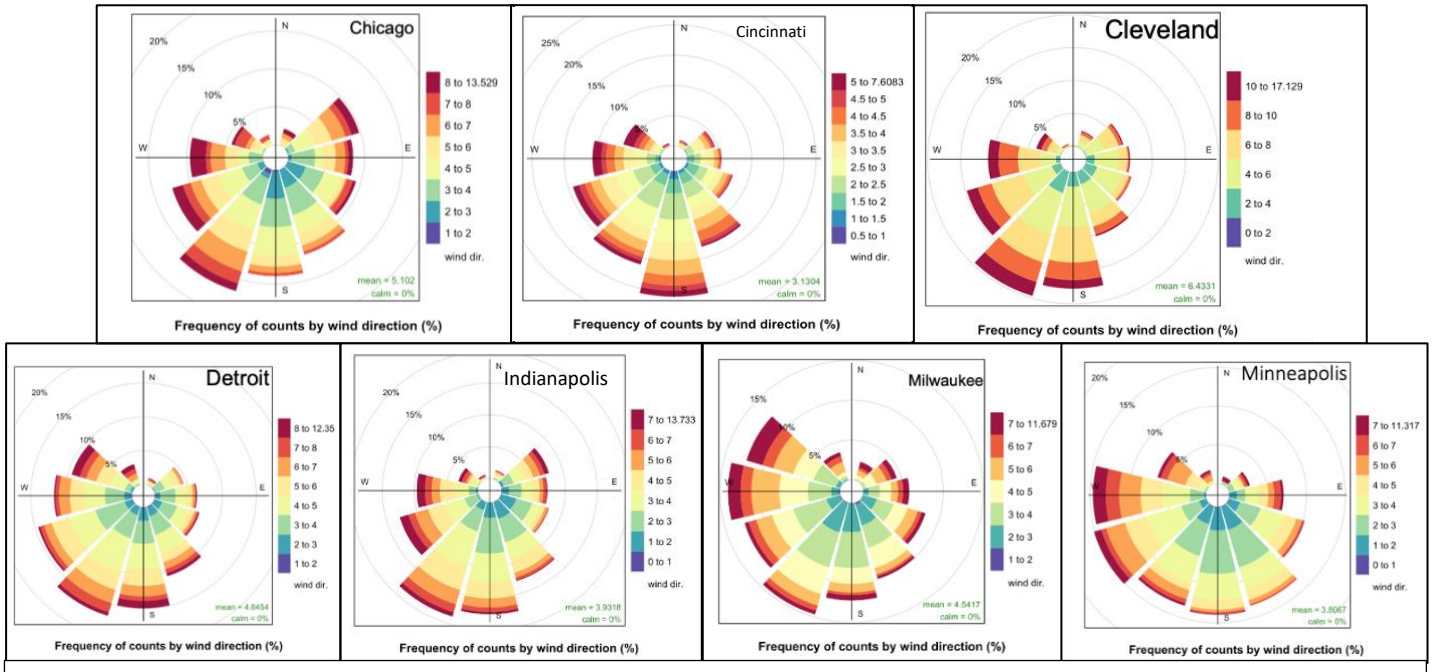

Figure 10. pollitionRose plots in 2018-2022 in Chicago, Cincinnati, Cleveland, Detroit, Indianapolis, Milwaukee and Minneapolis. The color range represents the level of $PM_{2.5}$ concentration.

The relationship between wind direction and $PM_{2.5}$ concentration are shown in Figure 10 in each city. By the length of each blade which represents the wind frequencies, we found winds were most frequently from south to southwest in Chicago, Cincinnati, Cleveland, Detriot, Indianapolis and Milwaukee, and in Minneapolis, winds most frequently blow from southeast to southwest to west. Also, by the colors which show $PM_{2.5}$ concentration levels, high PM2.5 concentrations mostly came from southwest to west in Chicago, Cincinnati, Indianapolis and Minneapolis, from south to west in Cleveland, from west to northwest in Milwauekee and from south and northwest in Detroit. Therefore, generally, in most days with high $PM_{2.5}$ concentration, wind blew from the west side (southwest or northwest) of the city.

4. Conclusions

In general, $PM_{2.5}$ concentration decreased dramatically over these 20 years, while it started to increase again recently. In this circumstance, EPA has proposed to lower the annual standard and is taking comments on lowering 24-hour standard (U.S. EPA, 2023).

In conceptual models, for chemical speciation, the dominant components in summer were OC in 2018-2022 and sulfate in 2000-2004. In winter, the dominant component was nitrate, in both periods. For meteorology, the higher wind speed is, the lower $PM_{2.5}$ concentration is and the higher temperature is, the higher $PM_{2.5}$ concentration is in summer. And the relationship between $PM_{2.5}$ concentration and relative humidity is negative in summer and positive in winter. Also, high $PM_{2.5}$ concentrations mostly came from west side of the city.

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