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Identification of potential source areas for elevated $PM_{2.5}$, nitrate and sulfate concentrations

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HIGHLIGHTS

► Effect of air parcel movements on variability in high $PM_{2.5}$ episodes is evaluated.
► Variations of air masses originating in high emission areas influence the episodes.
► Trajectories from the Ohio River Valley enhance major episode components.

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ABSTRACT

Extreme events or episodes of ambient fine particulate matter ($PM_{2.5}$), in which daily mass concentrations are substantially higher than annual averages, have been frequently observed in southern Wisconsin, US. Determining the cause of events has been a great challenge to local governments responsible for protecting public health and complying with the 24-h $PM_{2.5}$ standard. This study analyzed air parcel movements originating from emission source areas, and trends in $PM_{2.5}$ concentrations in order to determine the important factors involved in elevated $PM_{2.5}$ episodes in the region. A single backward trajectory analysis coupled with $PM_{2.5}$ concentrations observed at Federal Reference Method Network (FRM) sites in Madison, Milwaukee and Waukesha; and nitrate and sulfate concentrations monitored at a Chemical Speciation Network (CSN) site in Milwaukee, Wisconsin, from 2002 to 2010 were examined. The $PM_{2.5}$ concentrations from the FRM showed the total $PM_{2.5}$ mass during the episodes were higher in Madison than in Milwaukee and Waukesha, while annual average concentrations were lower in Madison. However, the temporal trend in frequency of elevated $PM_{2.5}$ episodes was remarkably similar across sites during the entire study period and high frequency episodes occurring from 2005 to 2007. Residence time analysis of backward trajectories calculated for all recorded data indicated episode changes were mainly driven by year-to-year variations of air mass movements originating in high emissions areas. Potential Source Contribution Function (PSCF) results showed the extreme events of $PM_{2.5}$ occurred during times when trajectories passed over ammonia emissions hotspots as well as large stationary emissions. Enhanced nitrate and sulfate concentrations which were the major episode components were strongly influenced by air masses trajectories originating from the Ohio River Valley and adjacent states.

1. Introduction

Ambient fine particulate matter ($PM_{2.5}$) is a major air quality concern because of its adverse health effects (Pope et al., 2009). To mitigate the health effects of $PM_{2.5}$, the United States Environmental Protection Agency (US EPA) promulgated the National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ in 1997. Due to the growing evidence of substantive health effects at low-to-moderate $PM_{2.5}$ concentrations which are common to many communities throughout the US (Pope and Dockery, 2006), the US EPA lowered the 24-h $PM_{2.5}$ standard from 65 $\mu g\ m^{-3}$ to 35 $\mu g\ m^{-3}$ in September 2006. The revised standard focuses on extreme events or episodes, in which daily mass concentrations are substantially higher than the annual average. Determining the causes of $PM_{2.5}$ episodes has been a great challenge to states, tribes and local governments that must comply with the tighter standard.

Elevated $PM_{2.5}$ episodes have been consistently observed at northern cities in the Midwest. In August 2011, the US EPA

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designated the southern Wisconsin area, including Milwaukee County, Racine County, and Waukesha County, as being in non-attainment of the 2006 $PM_{2.5}$ NAAQS. To provide a better understanding of the episodes and to create a strategic plan for compliance with the standard, a number of studies have been conducted and have concluded that specific meteorological conditions lead to high $PM_{2.5}$ episodes in this region. For example, the report of Conceptual Model of $PM_{2.5}$ Episodes in the Midwest (LADCO, 2009) stated the $PM_{2.5}$ episodes occur across broad areas in the upper Midwest and are mostly driven by stagnant air condition with high pressure, slow wind speeds, high relative humidity, and southerly winds. Katzman et al. (2010) reported elevated $PM_{2.5}$ episodes occur more often in winter than in summer at northern cities in the Midwest, and wintertime episodes are strongly enhanced by nitrate under a stagnation of weather patterns. de Foy et al. (2012) found that whereas black carbon is predominantly emitted by local sources, $PM_{2.5}$ has a more regional signature. Furthermore, Baek et al. (2010) showed wintertime episodes in the region are marked by inversions with a shallow, stable planetary boundary layer, warm, moist air and low wind speeds.

While the effect of meteorological conditions can provide a preliminary assessment of high $PM_{2.5}$ episodes, it is not enough to improve the understanding of important factors involved in the episodes. There is strong evidence that the long-range transport of air pollutants can increase gas and particle concentrations in urban and rural atmospheric environments. In some parts of the Midwest, $PM_{2.5}$ sulfate and nitrate concentrations have been influenced by the air masses and trajectories that originate in polluted upwind areas (Kim and Hopke, 2004; Lee and Hopke, 2006; Zhao and Hopke, 2006). Several counties in the Midwest may fail to comply with the current $PM_{2.5}$ standard due to the uncontrollable excess of $PM_{2.5}$ mass from outside the local boundary. To better understand elevated $PM_{2.5}$ episodes in non-attainment areas of southern Wisconsin, it is necessary to examine the effects of long-range transported pollutants and air mass movements on $PM_{2.5}$ concentrations.

Backward air trajectory analysis can be used to estimate the residence time that an air mass spends over each of specific source regions on its path to receptor sites. Statistical methods for combining measurements of pollutants and backward trajectories have been applied in many atmospheric studies to investigate the likely source regions and preferred transport directions that can contribute to elevated air pollutants at receptors sites (Ashbaugh et al., 1985; Vasconcelos et al., 1996; Polissar et al., 2001; Biegalski and Hopke, 2004; Zhou et al., 2004; Kim et al., 2005; Stohl et al., 2005; Zhao and Hopke, 2006; Lee and Hopke, 2006; de Foy et al., 2007; Zhao et al., 2007; Sunder Raman and Hopke, 2007; Chen et al., 2011; Gebhart et al., 2011; Hulkkonen et al., 2012). The Potential Source Contribution Function (PSCF) is a conditional probability of the statistical methods for mapping source areas of air masses related to high or low concentrations of air pollutants at sampling sites. PSCF has been employed as a relatively simple but valuable tool for identifying likely source locations of long-range transported air pollutants using a single air particle trajectory analysis (Ashbaugh et al., 1985; Polissar et al., 2001; Biegalski and Hopke, 2004; Kim et al., 2005; Lee and Hopke, 2006; Zhao and Hopke, 2006; Chen et al., 2011). Furthermore, a jointed PSCF method that multiples PSCF fields from multiple receptors in the back trajectory analysis has been shown to improve the resolution in source identification (Zeng and Hopke, 1989; Hsu et al., 2003a, 2003b; Lee and Ashbaugh, 2007).

As part of the US EPA fine particle monitoring network, $PM_{2.5}$ concentrations and components are measured around the US to determine compliance with the $PM_{2.5}$ NAAQS and to provide an understanding of the composition of sources of $PM_{2.5}$ at these monitoring locations. Measurements from southern Wisconsin show that $PM_{2.5}$ levels that are above daily high concentrations of $PM_{2.5}$ that impact both the annual average and 24-h $PM_{2.5}$ standards are strongly influenced by concentrations of secondary sulfate and nitrate. Moreover, there is a high correlation (i.e., $r = 0.97$) between the temporal variation of sulfate and nitrate at the two $PM_{2.5}$ Speciation sites in southern Wisconsin, Milwaukee and Waukesha, that are 27 km apart. A strong correlation indicates that the nitrate and sulfate concentrations are more influenced by regional transportation and less impacted by local emissions. To explore the effect of long-range transported pollutants on the $PM_{2.5}$ episodes in southern Wisconsin, this study looks at potential source areas using 9 years of measurements and the corresponding set of trajectories (i.e., approximately 25,000 trajectories per analysis). In addition, to further elucidate the role of air mass movements in the wintertime $PM_{2.5}$ episodes over the region, which have been recognized by several previous studies (Katzman et al., 2010 and references therein), joint PSCF analysis is conducted using 24-h $PM_{2.5}$ concentrations collected on a 1-in-3 day schedule at the Federal Reference Monitoring (FRM) sites in Madison, Waukesha, and Milwaukee from 2002 to 2010. This long-term data set makes it possible to trace back observed high $PM_{2.5}$ episodes across the study area. The results of the analysis can help to establish appropriate $PM_{2.5}$ control strategies.

2. Data and methods

2.1. Ambient samples

24-h $PM_{2.5}$ concentrations monitored at the FRM site in Madison (43.073 N, 89.436 W), Milwaukee (43.061 N, 87.912 W), and Waukesha (43.020 N, 88.215 W) from 2002 through 2010 were obtained from the US EPA Air Quality System (http://www.epa.gov/ttn/airs/airsaqs). All flagged data including machine malfunctions, power failures, invalid flow rates and other issues were reviewed and removed from the analysis. In addition, $PM_{2.5}$ mass data not matched with the 1-in-3 day sample duration between sites, especially the Madison site which recorded data every day after 2007, were eliminated to increase precision of the analysis. A total of 1019, 1028, and 1012 of the 24-h $PM_{2.5}$ data points in Madison, Waukesha, and Milwaukee, respectively, were considered in this analysis.

The Chemical Speciation Network (CSN) in the Milwaukee-Racine area in Wisconsin has two monitoring sites. One site is located in Milwaukee (43.061 N, 87.912 W), and the other site is in Waukesha (43.004 N, 88.232 W). The $PM_{2.5}$ speciation data including organic carbon (OC), elemental carbon (EC), nitrate, sulfate, ammonium, and other trace elements were collected on a 1-in-3 day schedule in Milwaukee and a 1-in-6 day schedule in Waukesha. The data from 2002 to 2010 at both sites were obtained from the US EPA AQS. To determine air mass origin for nitrate and sulfate, only the measurements at Milwaukee were considered as there were twice as many data points compared to Waukesha. A total of 1037 data points for the daily ion species in Milwaukee were used in the analysis.

2.2. Potential source contribution function (PSCF)

The PSCF model was applied to investigate the source regions which lead to elevated $PM_{2.5}$ episodes as well as enhanced nitrate and sulfate concentrations in southern Wisconsin. The back trajectories of air parcels were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT 4.9 version) using 80 km gridded meteorological data (EDAS 80 km) and 40 km gridded meteorological data (EDAS 40 km) for the ambient measurements from 2002 to 2004 and from 2005 to 2010, respectively (Draxler and Rolph, 2012). Five-day backward