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Formation of particulate sulfate and nitrate over the Pearl River Delta in the fall: Diagnostic analysis using the Community Multiscale Air Quality model

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HIGHLIGHTS

- The capability of CMAQ to reproduce $PM_{2.5}$ pollution in the Pearl River Delta (PRD) was assessed.
- Influences of different formation pathways of sulfate in PRD were quantified.
- Trans-boundary transport was the major source of sulfate over the PRD in the fall.
- The formation of nitrate over the PRD was limited by the availability of NH_3.

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ABSTRACT

In recent years, fine particulate matter (PM) pollution and visibility degradation have become severe air quality issues in China. In this study, $PM_{2.5}$ pollution over the Pearl River Delta (PRD) region during January, April, August, and November 2009 was simulated using the Community Multiscale Air Quality (CMAQ) model. An in-depth diagnostic analysis, focused on November 2009, was also conducted to reveal the patterns of sulfate and nitrate distribution, and to identify the main factors that influence the formation of sulfate and nitrate under typical meteorological conditions. The CMAQ model reasonably reproduced the observed concentrations, but showed better performance for January and November than it did for April and August, for which there was light-moderate underestimation of SO_2, NO_x, O_3, PM_{10}, and $PM_{2.5}$ concentrations, and slight overestimation of daily 8-h maximum concentrations of O_3. Utilizing a sulfate tracking technique, it was found that on nearly 20 days in November 2009, characterized by northeasterly winds, cross-boundary transport contributed to >75% of the total sulfate budget, while local gas phase oxidation and primary emissions averaged 10% and 8%, respectively. Aqueous sulfate typically contributed less than 1% of the total sulfate budget, except when the winds were directed from the sea and high humidity favored aqueous oxidation, and the percentage contribution reached up to 46%. NH_3 was generally sufficient to fully neutralize H_2SO_4; however, the formation of nitrate over the PRD was limited by the availability of NH_3.

1. Introduction

Sulfate and nitrate, largely present in the form of NH_4HSO_4, $(NH_4)_2SO_4$, and NH_4NO_3, are dominant inorganic aerosol species that account for ~30–60% of $PM_{2.5}$ (particulate matter with diameter less than 2.5 μm) mass concentrations (Sillanpää et al., 2006;

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Viana et al., 2007; Yang et al., 2011). They have an adverse effect on visibility, water body acidification, public health, and global climate change (Charlson et al., 1992; Dockery et al., 1996; Rodhe et al., 2002; Liu et al., 2012). Consequently, reductions in these two inorganic aerosols usually has significance for $PM_{2.5}$ pollution control and air quality improvement.

Although some source activities (e.g., industrial coal combustion) directly emit sulfates into the ambient atmosphere, most sulfates and nitrates form in the atmosphere through the oxidation of precursor gases, for example sulfur dioxide (SO_2) and nitrogen oxides (NOx), and then dynamically partition into aerosol phases following neutralization by ammonia (NH_3). The oxidation of SO_2 is typically much faster in aqueous phase than in gas phase, and sulfate production is mainly attributed to aqueous oxidation (Guo et al., 2010; Shen et al., 2012). Over the pH range of atmospheric interest (pH = 2–7), H_2O_2 is the dominant oxidant for SO_2 aqueous oxidation; O_3 becomes an important sulfur oxidant when the pH of cloud water is >5.5; and metal-catalyzed sulfur oxidation is generally of minor importance (Seinfeld and Pandis, 1998; Alexander et al., 2009; Bao et al., 2010; Shen et al., 2012). However, variations in oxidant concentrations, local sources, and meteorological conditions, may change the role of individual oxidation pathways in sulfate formation (Harris et al., 2012). Sulfate and nitrate concentrations are often enhanced by air mass contributions from polluted upwind areas (Revuelta et al., 2012). Sulfate contributors are largely the result of long-range transport, while nitrate is primarily derived from local or regional sources (Kwok et al., 2012; Squizzato et al., 2012; Brown et al., 2013). As a result of the non-liner response of sulfate and nitrate to the emissions of precursors, a decline in sulfate concentration may lead to a subsequent rise in nitrate levels (Metzger et al., 2002), or a reduction in NOx may unexpectedly enhance sulfate formation (Tsimpidi et al., 2008). Therefore, a thorough understanding of the processes involved in the formation and evolution of sulfate and nitrate is essential for developing effective control strategies for the management and mitigation of high inorganic aerosol levels.

In recent years, China has suffered from severe $PM_{2.5}$ pollution (Yang et al., 2011). Located in southeast China, the Pearl River Delta (PRD) region is densely populated. Intensive industry and heavy traffic resulted in high levels of $PM_{2.5}$ pollution (Wu et al., 2005; Zhang et al., 2008). Sulfate and nitrate are recognized as the major $PM_{2.5}$ components responsible for light extinction (Liu et al., 2012; Lin et al., 2013). At a rural site in Guangzhou, Xiao et al. (2011) observed increased concentrations of sulfate and ammonia in the daytime, driven by intensive photochemistry, and high nocturnal levels of nitrate due to enhanced gas-particle partitioning at lower temperature and higher relative humidity conditions. At another rural site downwind of the polluted central PRD area, Huang et al. (2011) found that even under high wind speed conditions, sulfate concentrations were maintained at moderate levels, reflecting the role of regional transport; however, due to air pollutant accumulation under calm air conditions, weak winds favored the gas-particle condensation of HNO_3. He et al. (2011) showed that short-range northeasterly transport was responsible for the high fraction of particulate nitrate in Shenzhen, a city located in the southern PRD. Field observations provide a direct insight into inorganic aerosol pollution at sampling sites; however, the processes governing the accumulation of sulfate and nitrate in the PRD remain unclear.

Long-term numerical simulations of $PM_{2.5}$ are limited in the PRD region (with the exception of Hong Kong), restricting the assessment of model performance. Consequently, the capability of air quality models in simulating $PM_{2.5}$ and its components requires further verification. In this study, the Model-3 Community Multiscale Air Quality (CMAQ) model (version 4.7.1) was employed to simulate $PM_{2.5}$ pollution over the PRD for January, April, August, and November 2009. In addition, a more detailed analysis of sulfate and nitrate pollution was conducted for November 2009, selected because PRD $PM_{2.5}$ episodes frequently occur in the fall (Feng et al., 2007; Huang et al., 2011; Kim et al., 2011). This study aims to examine the regional distribution of sulfate and nitrate, to identify the dominant formation pathways of sulfate, and to test the sensitivity of nitrate to emissions under varied meteorological conditions over the PRD.

2. Methodology

2.1. Model description and setup

The CMAQ model (Byun and Schere, 2006; Eder and Yu, 2006; Yu et al., 2012; Yu et al., 2014) version 4.7.1, utilizing the SAPRC99 gas-phase chemistry mechanism (Carter, 2000) and the AERO5 aerosol module (Binkowski and Roselle, 2003), was employed to simulate $PM_{2.5}$ pollution over the PRD region for January, April, August, and November 2009. The three nested grid resolutions (36 km, 12 km, and 4 km) were used and the innermost domain covers the whole PRD region (Fig. 1a). There were 13 vertical layers extending up to 50 mb under the sigma-P coordinate system. The meteorological fields were provided by Weather Research and Forecast (WRF) version 3.2 and emission data was processed by Sparse Matrix Operator Kernel Emissions (SMOKE) version 2.5. Specifically, emissions of anthropogenic sources for the domains at 36 km and 12 km resolution were derived from the 2006 Asian INTEX-B emission inventory (Zhang et al., 2009), with NH_3 emission data from the 2000 Trace-P inventory (Streets et al., 2003). Anthropogenic emission data for the innermost domain were developed on the basis of the 2006 PRD regional emission inventory (Zheng et al., 2009). Moderate Resolution Imaging Spectroradiometer (MODIS) land use data was imported and processed by Biogenic Emissions Inventory System (BEIS) version 3.14 in order to create model-ready biogenic emissions estimates.

2.2. Model evaluation protocol

Predicted meteorological fields (including temperature, humidity, wind direction, and wind speed) were compared with the hourly observations, extracted from dataset ds461.0 of the U.S. NCEP ADP Global Surface Observational Weather Data.[1] Performance statistics were calculated using the Metstat Statistical Analysis Package (Emery et al., 2001).

To assess the performance of CMAQ, metrics including Normalized Mean Error (NME), Normalized Mean Bias (NMB), and correlation coefficient (r), which are defined in Yu et al. (2006), were calculated. Hourly observational data of criteria pollutants, including SO_2, NO_2, O_3, and PM_{10}, were obtained from the PRD Regional Air Quality Monitoring Network, which consists of 17 stations (Fig. 1b). Of the 17 stations, hourly measurements of $PM_{2.5}$ were available at 3 Hong Kong stations. Additionally, $PM_{2.5}$ and its components (including SO_4^{2-}; NO_3^-; NH_4^+; organic carbon, OC; and elemental carbon, EC) were measured at 6 Shenzhen stations (Fig. 1b), with varying sampling frequency (Table S1). The detailed analytical methods were as described by Yun et al. (2013).

[1] National Centers for Environmental Prediction/National Weather Service/NOAA/U.S. Department of Commerce (2004): NCEP ADP Global Surface Observational Weather Data, October 1999–continuing. Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory. http://rda.ucar.edu/datasets/ds461.0/. Accessed 11 Jan 2014.