Science of the Total Environment 490 (2014) 171–181

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Source apportionment of sulfate and nitrate particulate matter in the Eastern United States and effectiveness of emission control programs

Hongliang Zhang [a,1], Jianlin Hu [b], Michael Kleeman [b], Qi Ying [a,*]

[a] Zachry Department of Civil Engineering, Texas A&M University, College Station, TX, USA
[b] Department of Civil and Environmental Engineering, University of California, Davis, CA, USA

HIGHLIGHTS

- Source contributions to secondary nitrate and sulfate in the eastern US were determined.
- Coal combustion and natural gas burning were major sources of sulfate.
- Vehicles, coal and natural gas burning were major sources of nitrate.
- Assessing the magnitude of control benefits needs to consider changes in meteorology.

ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 13 April 2014
Accepted 16 April 2014
Available online xxxx

Editor: Xuexi Tie

Keywords:
Source apportionment
Sulfate
Nitrate
Eastern US
CMAQ
Emission controls

ABSTRACT

Reducing population exposure to $PM_{2.5}$ in the eastern US will require control of secondary sulfate and nitrate. A source-oriented Community Multi-scale Air Quality (CMAQ) model is used to determine contributions of major emission sources to nitrate and sulfate concentrations in the seven eastern US cities (New York City, Pittsburgh, Baltimore, Chicago, Detroit, St. Paul, and Winston-Salem) in January and August of 2000 and 2006. Identified major nitrate sources include on-road gasoline-powered vehicles, diesel engines, natural gas and coal combustion. From 2000 to 2006, January nitrate concentrations decreased by 25–68% for all the seven cities. On average, ~53% of this change was caused by emissions controls while 47% was caused by meteorology variations. August nitrate concentrations decreased by a maximum of 68% in New York City but Detroit experienced increasing August nitrate concentrations by up to 33%. On average, ~33% of the reduction in nitrate is offset by increases associated with meteorological conditions that favor nitrate formation. Coal combustion and natural gas are the dominant sources for sulfate in both seasons. January sulfate decrease from 2000 to 2006 in all cities by 4–58% except New York City, which increases by 13%. On average, ~93% of the reduction in sulfate was attributed to emission controls with 7% associated with changes in meteorology. August sulfate concentrations decrease by 11–44% in all cities. On average, emission controls alone between 2000 and 2006 would have caused 6% more reduction but the effectiveness of the controls was mitigated by meteorology conditions more favorable to sulfate production in 2006 vs. 2000. The results of this study suggest that regional emissions controls between 2000 and 2006 have been effective at reducing population exposure to $PM_{2.5}$ in the eastern US, but yearly variations in meteorology must be carefully considered when assessing the exact magnitude of the control benefits.

1. Introduction

Airborne particulate matter (PM) is a complex mixture of small particles and liquid droplets suspending in the atmosphere that can be emitted directly as primary PM or formed through gas-to-particle partitioning of semi-volatile products as secondary PM. In addition to its impacts on radiation balance and climate by directly absorbing and/or scattering incoming solar radiation (Charlson et al., 1992; Kiehl and Briegleb, 1993) and by indirectly acting as cloud condensation nuclei (CCN) (Cruz and Pandis, 1997; Jones et al., 1994), PM also adversely affects human health (Laden et al., 2006; Moolgavkar and Luebeck, 1996; Pope and Dockery, 2006; Schwartz et al., 2002) and thus life expectancy (Pope et al., 2009).

The eastern United States (US) experiences high PM concentrations by the North American standards (EPA, 2004). Based on the 2006 National Ambient Air Quality Standards (NAAQS) for 24-hour $PM_{2.5}$ mass concentration, 59 counties in 10 states in the eastern US are designated as non-attainment by the US Environmental

* Corresponding author. Tel.: +1 979 845 9709; fax: +1 979 862 1542.
E-mail address: qying@civil.tamu.edu (Q. Ying).
[1] Currently address: Department of Civil and Environmental Engineering, University of California, Davis, USA.

http://dx.doi.org/10.1016/j.scitotenv.2014.04.064
0048-9697/

Protection Agency (EPA) (http://www.epa.gov/pmdesignations/2006standards/documents/finaltable2011.htm), and numerous epidemiological studies have related population health outcomes with particulate air pollution exposure in the eastern US (Bell et al., 2007; Dominici et al., 2006; Samet et al., 2000). Ammonium sulfate and nitrate are the major chemical components of PM in the eastern US, accounting for more than half of the $PM_{2.5}$ mass concentrations (EPA, 2004, 2012; Fine et al., 2008; Luo et al., 2011; Walker et al., 2012). Analyses of measurement data throughout the country reveal that particulate sulfate and nitrate have clear seasonal patterns. Sulfate (from SO_2 emissions) is more readily formed in the eastern US in summertime (July to September) while particulate nitrate (from NO_x emissions) concentrations are higher in cooler weather. These trends reflect the balance between precursor emissions rates, chemical reaction rates, and equilibrium partitioning between the gas and condensed phases.

The relationship between secondary PM component concentrations and the emission rates of their primary precursors from different source categories needs to be studied in order to determine the contributions of different emission sources to secondary PM concentrations and adverse health effects, and to design more efficient emission control strategies. Different statistical and mechanistic methods have been developed for source apportionment studies. Statistical models such as chemical mass balance (CMB) and positive matrix factorization (PMF) are more useful for primary pollutants (Held et al., 2005; Norris et al., 2008). Sensitivity analysis methods such as Brute Force Method (BFM) and decoupled direct method (DDM) can be used to determine the relative importance of the emission from different sources, however, they are not able to quantify the total source contributions because the effects of local emissions perturbations cannot be accurately extrapolated in the non-linear chemical reaction system (Berglen et al., 2004; Liu et al., 2008). A rigorous approach that tracks the source contributions to both primary and secondary PM is the source-oriented external mixture (SOEM) method described by Mysliwiec and Kleeman (2002) and applied in 3D models (Ying and Kleeman, 2006; Zhang et al., 2014b). The SOEM method tracks gaseous precursor emissions from different source categories and their reaction products separately to retain source information. Particles are represented as external mixtures to determine contributions to primary PM. A simplified approach that utilizes source-oriented representation of gas phase emissions, chemical transformations and gas-to-particle partitioning of semi-volatile products but treats particles as internal mixtures has been implemented in the widely used Community Multi-scale Air Quality (CMAQ) model developed by the US EPA. The expanded source-oriented CMAQ model has been applied to study source contributions to secondary PM in Texas (Zhang and Ying, 2011, 2012) and China (Wang et al., submitted for publication; Zhang et al., 2012). An alternative approach that determines the changes of the tracer concentrations at each time step using process analysis information and mass balance analysis instead of directly solving their concentrations based on the differential equations has also been proposed as a means to increase computation efficiency in source apportionment calculations (Wagstrom et al., 2008; Wang et al., 2009).

While a number of models are available for source apportionment of secondary $PM_{2.5}$ nitrate and sulfate, none of the models have been applied to extensively study the source contributions to sulfate and nitrate in the eastern US for periods long enough that include different meteorology and emission conditions. The objective of this study is to apply a source-oriented 3D regional chemical transport model to determine the source contributions of nitrate and sulfate in the eastern US with a focus on the seven urban areas in that region using four month-long PM modeling episodes, January and August of 2000 and 2006. The study also evaluates the importance of regional transport, changes in direct emissions and variations in meteorology conditions on $PM_{2.5}$ sulfate and nitrate concentrations in the eastern US.

2. Model description

In this study, a source-oriented version of the CMAQ model (based on CMAQ version 4.7.1) (Byun and Schere, 2006; Carlton et al., 2010) was applied to directly track precursors of sulfate and nitrate from various emission sources and determine their contributions to sulfate and nitrate concentrations. The detail of the source apportionment technique for secondary PM has been documented by Ying and Kleeman (2006) and its implementation in the CMAQ model has been reported in a previous publication (Zhang et al., 2012), thus only a short summary is provided here. The SAPRC-99 photochemical mechanism (Carter, 2000) was modified to include additional reactions and species so that NO_x and SO_2 and their gas phase reaction products from different sources are separately tracked with source-tagged species. For example, model species SO2_X1 and SO2_X2 are used to represent SO_2 from two different sources. The current version of the modified SAPRC-99 mechanism with 304 gas phase species and 2000 gas phase reactions in the source-oriented CMAQ model can track up to 9 sources simultaneously in a single simulation. The SMVGEAR solver in the CMAQ distribution is

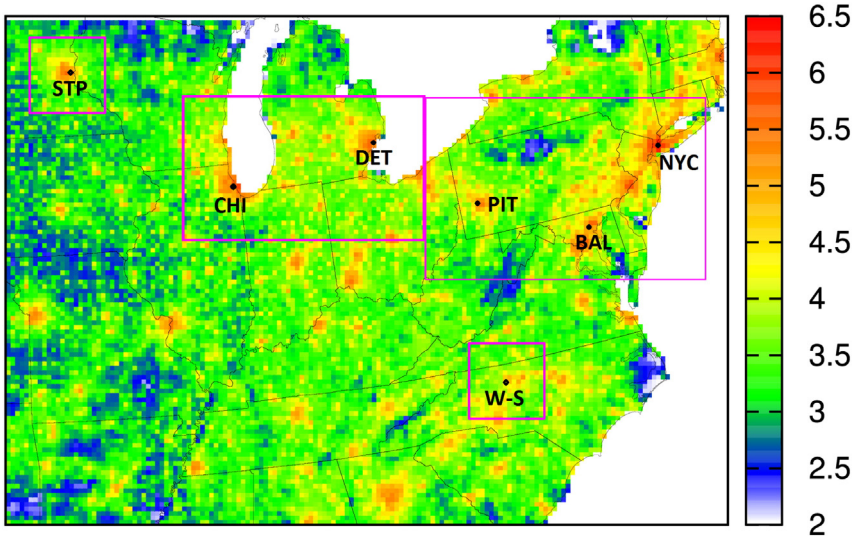

Fig. 1. The 12-km eastern US domain and the population density (per grid cell, in log-10 scale) in the area. The 36-km domain, which covers the entire continental US and part of Canada and Mexico, is not shown. The purple boxes are the nested 4-km domains. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)