Atmospheric Environment 45 (2011) 223–234

Contents lists available at ScienceDirect

Atmospheric Environment

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

Modeling the fate of atmospheric reduced nitrogen during the Rocky Mountain Atmospheric Nitrogen and Sulfur Study (RoMANS): Performance evaluation and diagnosis using integrated processes rate analysis

Marco A. Rodriguez [a,*], Michael G. Barna [b], Kristi A. Gebhart [b], Jennifer L. Hand [a], Zachariah E. Adelman [c], Bret A. Schichtel [b], Jeffrey L. Collett Jr. [d], William C. Malm [a]

[a] Cooperative Institute for Research in the Atmosphere, Colorado State University, 1375-Campus Delivery, Fort Collins, CO 80523-1375, USA
[b] Air Resources Division, National Park Service, Fort Collins, CO 80523-1375, USA
[c] Institute for the Environment, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-6116, USA
[d] Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA

ARTICLE INFO

Article history:
Received 21 May 2010
Received in revised form
18 August 2010
Accepted 3 September 2010

Keywords:
Ammonia
Reduced nitrogen
CAMx
Process analysis
RoMANS
Rocky Mountain National Park

ABSTRACT

Excess wet and dry deposition of nitrogen-containing compounds is a concern at a number of national parks. The Rocky Mountain Atmospheric Nitrogen and Sulfur Study (RoMANS) was conducted during the spring and summer of 2006 to identify the overall mix of ambient and deposited sulfur and nitrogen at Rocky Mountain National Park (RMNP), in north-central Colorado. The Comprehensive Air Quality Model with extensions (CAMx) was used to simulate the fate of gaseous and particulate species subjected to multiple chemical and physical processes during RoMANS. This study presents an operational evaluation with a special emphasis on the model performance of reduced nitrogen species. The evaluation showed large negative biases and errors at RMNP and the entire domain for ammonia; therefore the model was considered inadequate for future source apportionment applications. The CAMx Integrated Processes Rate (IPR) analysis tool was used to elucidate the potential causes behind the poor model performance. IPR served as a tool to diagnose the relative contributions of individual physical and chemical processes to the final concentrations of reduced nitrogen species. The IPR analysis revealed that dry deposition is the largest sink of ammonia in the model, with some cells losing almost 100% of the available mass. Closer examination of the ammonia dry deposition velocities in CAMx found that they were up to a factor of 10 larger than those reported in the literature. A series of sensitivity simulations were then performed by changing the original deposition velocities with a simple multiplicative scaling factor. These simulations showed that even when the dry deposition values were altered to reduce their influence, the model was still unable to replicate the observed time series; i.e., it fixed the average bias, but it did not improve the precision.

1. Introduction

Excess wet and dry deposition of nitrogen-containing compounds, such as nitric acid (HNO_3), particulate ammonium (NH_4^+), particulate nitrate (NO_3^-), and ammonia (NH_3), is a concern at a number of national parks. Rocky Mountain National Park (RMNP), in north-central Colorado, provides a well-documented example of the role of excess nitrogen deposition in sensitive alpine environments and its potential to influence ecosystem dynamics (Baron, 2006; Baron et al., 2000; Korb and Ranker, 2001; Nydick et al., 2004). Human activity, including combustion of fossil fuels, application of nitrogen fertilizers, confined animal feedlot operations (CAFO), and cultivation of nitrogen-fixing legumes, has substantially altered the global nitrogen cycle (Galloway et al., 2003). Wet and dry deposition of reduced nitrogen ($N(-III) = NH_3 + NH_4^+$) and atmospheric oxidation products of nitrogen oxides ($NO_x = NO + NO_2$) are significant nitrogen inputs in many environments.

To investigate nitrogen deposition at RMNP, and to elucidate the nitrogen sources that are impacting the park, the National Park Service initiated the Rocky Mountain Atmospheric Nitrogen and Sulfur Study (RoMANS) (Beem et al., 2010; Malm et al., 2009; Levin et al., 2009). The RoMANS study included two 5-week sampling periods in 2006. The first was a spring campaign from March 23

* Corresponding author. Tel.: +1 970 491 8101; fax: +1 970 491 8598.
E-mail address: rodriguez@cira.colostate.edu (M.A. Rodriguez).

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doi:10.1016/j.atmosenv.2010.09.011

through April 30 and the second a summer campaign from July 6 through August 12. Upslope easterly flow that can bring emissions from the east (the Front Range region – which includes the Denver metropolitan area – and beyond) is more common during hours of precipitation than during non-precipitating hours for all seasons. However, climatologically, wet deposition during spring and summer is associated with precipitation from different types of meteorological regimes. Spring precipitation is mostly due to large-scale storms associated with widespread regional precipitation, while summer precipitation is mostly due to small-scale afternoon convective activity due to air masses rising over the mountains. The frequency of easterly flow when precipitation also occurs is greater during spring than summer, but the vertical depth of easterly flow is often greater during summer than spring.

CAMx (Comprehensive Air Quality Model with extensions version 4.51; ENVIRON, 2005), an advanced eulerian chemical transport model (CTM), was used to simulate the ambient concentrations of nitrogen and sulfur species during the two RoMANS sampling periods. Although CAMx has been used extensively to simulate regional sulfate and ozone (Yarwood et al., 2003; Morris et al., 2004), and to a lesser degree nitrate and nitric acid (Baker and Scheff, 2007), its application to modeling ammonia and organic nitrogen in regions of complex terrain has been limited. As part of RoMANS, the National Park Service had great interest in conducting the current modeling effort with the original intent to provide greater insight into the source types and regions that contribute the most to nitrogen deposition, especially NH_3, at RMNP. The source apportionment analysis can be reliable only if a performance evaluation of the regional modeling system properly assesses the suitability of the model to this type of application (Barna et al., 2006; Jiménez et al., 2006; Morris et al., 2006; Pun et al., 2006; Tesche et al., 2006; Tonnesen et al., 2006). The first part of this study provides an operational model evaluation with special emphasis on the model performance of reduced nitrogen species. This evaluation relies on the RoMANS dataset, which is unique in that it provides high time resolution measurements of NH_3, a species not routinely measured, at the core site located in RMNP. Realizing that the model performance for reduced nitrogen, but especially NH_3, leaves the model unsuitable for source apportionment applications, the second part of this work concentrates on a model diagnosis to investigate the underlying causes of this poor performance. The CAMx 'integrated processes rate analysis' tool was used for an in-depth analysis of the model performance and to reveal the relative contributions from individual physical and chemical processes (e.g., emissions, chemistry, deposition, and transport) to the predicted concentrations of nitrogen species. Finally, guided by the process analysis results, the effects of different deposition velocities on the predicted NH_3 concentrations were investigated through a series of sensitivity simulations where a simple multiplicative factor modifies the original deposition velocities values.

2. Modeling system description

The air quality modeling system consisted of three major components: CAMx, a CTM; the Penn State University/NCAR Mesoscale Model (known as MM5), a regional weather model (Grell et al., 1994); and SMOKE (Sparse Matrix Operator Kernel Emissions; Houyoux et al., 2002; IE, 2006), an emissions processing system that transforms emissions inventory data to the chemical, spatial, and temporal terms required by the CTM. CAMx was run with two-way grid nesting, using three domains with horizontal grid size resolutions of 36 km, 12 km, and 4 km (Fig. 1). The 36-km outer domain covered the contiguous United States, southern Canada, and northern Mexico. The 4-km inner domain extends over most of Colorado, and the 12-km domain encompassed the surrounding states. The horizontal model domains were specified using an 'Arakawa C' grid, and sigma pressure levels were used in the vertical dimension.

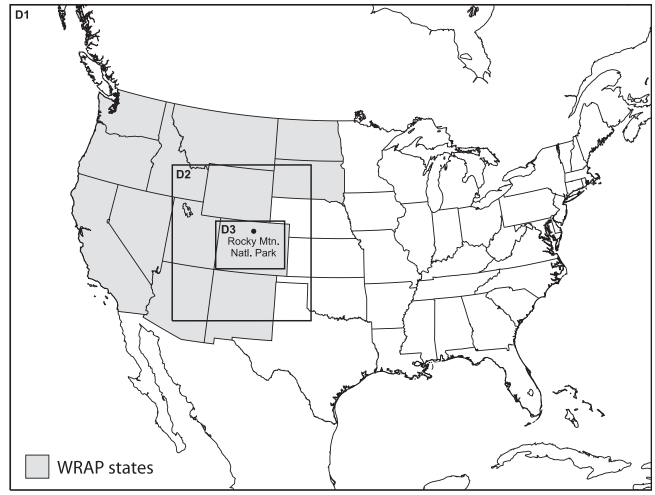

Fig. 1. Map of the three nested computational domains used in this study. The outer domain (D1) covers the contiguous United States, northern Mexico and southern Canada with a horizontal grid resolution of 36 km. The inner domain (D3) extends over most of Colorado with a grid resolution of 4 km, while D2 encompasses the surrounding states with a grid resolution of 12 km. The states in gray are part of the Western Regional Air Partnership (WRAP) regional planning organization.

Horizontal advection was treated with the piecewise-parabolic method (PPM), an area-preserving, flux-form advection solver with explicit horizontal diffusion (Odman and Ingram, 1996). Gas-phase chemistry was based on the Carbon Bond IV mechanism (Whitten et al., 1996). ISORROPIA (version 1.6), a thermodynamic equilibrium model (Nenes et al., 1999), was used to predict the partitioning of inorganic aerosol constituents (sulfate, nitrate, and ammonium) between the gas and particle phases. CAMx represents aerosol size distributions with a sectional approach, and in particular this study used the CF scheme that divides the size distribution into two static modes (coarse and fine). The CAMx outputs include hourly average concentrations for gas and particulate species. MM5 provided the wind fields that CAMx needed to determine the transport of chemical species, as well as other meteorological variables such as temperature, pressure, and precipitation.

The SMOKE processing system was used to prepare the emissions inventory data in a prescribed format that reflected the spatial, temporal, and chemical speciation parameters required by CAMx on the RoMANS nested domains (Fig. 1). Developing an approach to estimate air pollutant emissions that were representative of the RoMANS field study period was necessary since 2006 inventory data were not readily available for North America at the time this study took place. For most of the emissions sectors, such as on-road mobile and stationary area sources, inventories developed by the U.S. Regional Planning Organizations (RPOs) to support regional haze state implementation plan (SIP) modeling were used (Morris et al., 2007; Pechan, 2003). In particular, the inventories and methodologies developed by the Western Regional Air Partnership (WRAP) were employed as a starting point for developing the RoMANS inventory (Tonnesen et al., 2006). The emissions database was built using the WRAP inventory developed for 2002 and that consists of 22 different categories (e.g., automobiles, power plants, forest fires, oil and gas development, etc.). Given the potentially large contribution of NH_3 to overall nitrogen deposition at RMNP, the WRAP NH_3 emissions inventory was updated in an attempt to capture the local and regional NH_3 emissions patterns