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Source–receptor relationships of nitrate in Northeast Asia and influence of sea salt on the long-range transport of nitrate

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HIGHLIGHTS

- Source–receptor relationship of total deposition of nitrate (TDN) in Northeast Asia.
- 95% of TDN across China consisted of contributions from Chinese emissions.
- Chinese emissions contributed TDN by 50–75% over the downwind regions.
- Presence of sea-salt particles increased TDN by 10–40% over the downwind regions.

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ABSTRACT

We conducted a source–receptor relationship (SRR) analysis of the total deposition of nitrate (TDN; dry + wet, gas + aerosol) in Northeast Asia using an aerosol chemical transport model. Six regions were included in the study: North China, Central China, South China, South Korea, Japan, and Ocean. More than 95% of the TDN across China consisted of contributions from Chinese emissions. The largest intra-regional contributions and the second largest contributions were attributed to the Central China region. The contribution of the three China regions accounted for approximately 50–60% of the TDN in South Korea and Japan and 75% of the TDN in the Ocean region, respectively. The spatial distributions of the SRR indicated that the sub-regional high was more than twice the regional averages of the TDN. We also investigated the effects of sea salt on the transport and deposition of nitrate. During the long-range transport from the Asian continent over the ocean, nitric acid gas condenses on sea-salt particles to form $NaNO_3$. The presence of sea-salt particles increased the TDN over the downwind regions of the Asian continent by approximately 10–25% in South Korea and Japan and by up to 40% in the Ocean region. However, the sea-salt effects on the SRR of the TDN were small (the absolute differences were smaller than approximately 10%).

1. Introduction

Nitric acid is an important acidic substance in the atmosphere. The East Asian region has been one of the largest sources of the emission of its precursor, NO_x (Streets et al., 2003; Ohara et al., 2007; Zhang et al., 2009). To better understand the trans-boundary transport of air pollutants and to plan environmental policies, inter-political and inter-regional source–receptor relationship (SRR) analyses have been widely conducted (e.g., Carmichael et al., 2002; Holloway et al., 2002; Lin et al., 2008; Nagashima et al., 2010; Kajino et al., 2011; Inomata et al., 2013). Because nitrate chemistry involves highly nonlinear photochemical chain reactions between NO_x, VOCs, and O_x, several techniques have been established to study the SRRs of nitrates (Bartinicki, 1999; Holloway et al., 2002; Lin et al., 2008; Nyiri et al., 2010). Nitric acids are semi-volatile and partitioned into gas and aerosol phases in the troposphere. Because dry deposition and wet scavenging mechanisms are different for nitrates in the gas and aerosol phases, the accurate prediction of the gas-aerosol partitioning is important for the prediction of the deposition amounts (Kajino et al., 2005, 2008; Kajino and Ueda, 2011). Modeling the wet deposition amounts is also difficult due to the large uncertainties associated with the prediction of aerosol activation and cloud microphysical and dynamical processes. As the result of all of these complexities, there have been discrepancies of one to two orders of magnitude in the monthly mean wet deposition amounts predicted

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by several regional-scale models (Wang et al., 2008). To reduce these uncertainties and to better estimate the impact of transboundary air pollution problems, the importance of the model ensemble technique has been highlighted in model intercomparison studies (Carmichael et al., 2002, 2008; Choi et al., 2001; Kim et al., 2011, 2012). The ensemble mean prediction, which is a simple average of all the different model results, agreed well with the observation data (Wang et al., 2008).

In the current study, we estimated the SRR of the total deposition of nitrate (TDN; the dry and wet depositions of nitrate in the gas and aerosol phases) using an Eulerian regional-scale aerosol chemical transport model denoted Regional Air Quality Model 2 (RAQM2; Kajino et al., 2012a). RAQM2 incorporates a fully dynamical triple-moment modal aerosol microphysics module (Kajino, 2011). The model's performance has been evaluated in terms of the size distributions and mixing types of inorganics (Kajino and Kondo, 2011; Kajino et al., 2012a) and the wet deposition amounts (Kajino et al., 2012b) in Northeast Asia. To show the validity of our SRR estimation, the modeled concentrations and wet deposition amounts were compared with monitored data from six remote stations of the Acid Deposition Monitoring Network in East Asia (EANET). The SRR results were also compared with that obtained in the previous studies conducted by Lin et al. (2008) and Holloway et al. (2002), who used an Eulerian chemical transport model (CMAQ) and a Lagrangian puff model (ATMOS-N), respectively, to detect the differences between the different methods.

There are two other important aspects of the study: the spatial distribution of the SRR and the effects of sea salt. The SRR is usually discussed based on regional averages. However, sub-regional variations are also important because the sub-regional maxima are approximately two times larger than the regional averages due to non-uniformity across the deposition fields (Kajino et al., 2011). Nitric acid gas strongly interacts with sea-salt particles. During long-range transport from the Asian continent over the ocean toward Korea and Japan under the influence of the mid-latitude westerlies, nitric acid gas condenses onto sea-salt particles, reacts with NaCl, and is fixed in the aerosol phase as $NaNO_3$. Our previous studies, which are based on observations as well as simulations, indicated that approximately 50% of nitrate is mixed with sea-salt particles in Korea (Kajino and Kondo, 2011) and that more than 90% is mixed with sea-salt particles over the remote island in Japan (Kajino et al., 2012a). Because some of the previous models in Holloway et al. (2002), Lin et al. (2008), and Carmichael et al. (2008), did not consider the interaction between nitric acid and sea-salt particles over Northeast Asia, we focused on the effect of sea-salt particles on the deposition of nitrate and the SRR of TDN.

2. Methods

2.1. Numerical model and the SRR method

An offline coupled chemical transport model, which is denoted the Regional Air Quality Model (RAQM2; Kajino et al., 2012a), was used. The Advanced Research Weather Research and Forecasting (WRF) model (version 3.1.1; Skamarock et al., 2008) was used to simulate the meteorological field. The US National Center for Environmental Prediction (NCEP; 6 h, 1°×1°) final operation global analysis dataset (ds083.2; http://dss.ucar.edu/datasets/ds083.2) was used for the initial and boundary conditions for the WRF. The analysis data were also used for the nudging method.

The RAQM2 utilizes a multi-category approach to describe the aerosol mixing state; in this approach, the aerosols are distributed into four categories: Aitken mode (ATK), soot-free accumulation mode (ACM), soot aggregates (AGR), and coarse mode (COR). The RAQM2 achieved a completely dynamic (non-equilibrium) solution for the gas-to-particle mass transfer and the Brownian coagulation over a wide range of aerosol diameters (from 1 nm to super μm) using the triple moment Modal Aerosol Dynamics model for multiple Modes and fractal Shapes (MADMS; Kajino, 2011). The simulation settings, such as the domain size, grid numbers, and resolution ($100 \times 70 \times 19$, $\Delta x = 60$ km with Lambert conformal, as shown in Fig. 1), and the chemical and physical sub-modules are almost identical to those described by Kajino et al. (2012a, 2012b) and are thus not described here, with the exception of the emission inventory and the sensitivity simulations used in the source–receptor relationship (SRR) analysis.

The simulation was conducted within the framework of a model inter-comparison study for the Long-range Transboundary Air Pollutants in Northeast Asia (LTP project) among China, Korea, and Japan (Choi et al., 2001; Kajino et al., 2011; Kim et al., 2011, 2012). We used the anthropogenic emissions measured by Zhang et al. (2009) from China, North Korea, South Korea, Taiwan, and Japan with the base year of 2006 and monthly variations. We used the Global Fire Emission Database (GFED3; Giglio et al., 2010) for the monthly mean open biomass burning emissions and the Model of Emission of Gases and Aerosols from Nature (MEGAN2; Guenther et al., 2006) for the

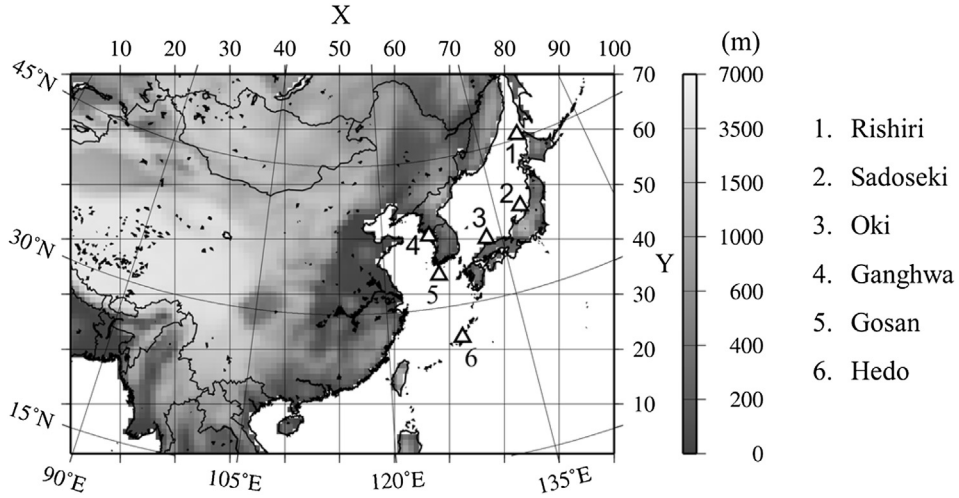

Fig. 1. Modeling domain ($X = 100$, $Y = 70$, $\Delta X = \Delta Y = 60$ km, Lambert conformal map projection) showing the terrestrial elevation (m) and the EANET monitoring sites (triangles; 1. Rishiri, 2. Sadoseki, 3. Oki, 4. Ganghwa, 5. Gosan, and 6. Hedo). The locations of the EANET stations are given in Table 1.