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Impacts of aerosols on surface-layer ozone concentrations in China through heterogeneous reactions and changes in photolysis rates☆

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HIGHLIGHTS

- We have examined the spatial and temporal variations of aerosol impacts on O_3.
- We have quantified the role of each and all heterogeneous reactions.
- Heterogeneous reactions reduce O_3 in eastern China by 10–18% on an annual mean basis.
- Concentration of O_3 in Pearl River Delta is most sensitive to the impacts of aerosols.

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ABSTRACT

We quantify the impacts of aerosols on distributions and concentrations of O_3 over China through heterogeneous reactions and changes in photolysis rates using the global chemical transport model GEOS-Chem. Aerosols considered include sulfate, nitrate, ammonium, organic carbon, and black carbon. Consideration of the impacts of aerosols improves the simulated O_3 concentrations in China; the averaged biases in simulated O_3 concentrations in China are +9% and +33% with and without the impacts of aerosols, respectively. The impacts of heterogeneous reactions on O_3 are simulated to exhibit large spatial and temporal variations, and those of aerosols through altering photolysis rates are simulated to be small. Accounting for hydrolysis of N_2O_5, irreversible absorption of NO_2 and NO_3 on wet aerosols, and the uptake of HO_2 by aerosols, O_3 concentrations are simulated to decrease by 8–12 ppbv in northern China and to increase by 3–6 ppbv in southern China in winter, and reductions in O_3 of exceeding 6 ppbv are simulated in a large fraction of China in other seasons. With the assumed uptake coefficients in this work, the hydrolysis of N_2O_5 is simulated to have a dominant role in reducing O_3 concentrations all over China, as a result of the large reductions in NO_x in the lower to middle troposphere in the northern mid-latitudes. On the contrary, the absorption of NO_2 and NO_3 is found to increase O_3 concentrations by 3–10 ppbv in eastern China in winter because of the increases in chemical production of O_3 in the VOC-limited regions. The impact of aerosols on O_3 concentration through heterogeneous reactions is characterized in this work by the ratio of change in O_3 concentration to local $PM_{2.5}$ level (ROP = $\Delta[O_3]/[PM_{2.5}]$). The locations of maximum reductions in O_3 are not necessarily the places of maximum aerosol concentrations; the annual mean values of ROP are calculated to be −0.14, −0.17, −0.27, and −0.16 ppbv $(\mu g\ m^{-3})^{-1}$ over the heavily polluted regions of Beijing–Tianjin–Tanggu, Yangtze River Delta, Pearl River Delta, and Sichuan Basin, respectively. Values of ROP are determined by both local heterogeneous reactions and transport of O_3 from surrounding areas.

1. Introduction

Tropospheric O_3 and aerosols are major air pollutants in the atmosphere that have adverse effects on human health, crops, plants, and atmospheric visibility. They have also made significant contributions to radiative forcing of climate since preindustrial time (Intergovernmental Panel on Climate Change (IPCC), 2007).

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Concentrations of tropospheric O_3 and aerosols are coupled through the formation and growth of aerosols, heterogeneous reactions, and aerosol-induced changes in photolysis rates. With the rapid urbanization and economic development, observed aerosol concentrations are especially high in China (Cao et al., 2007; Andreae et al., 2008; Gu et al., 2011; Zhang et al., 2012), suggesting that aerosols in China can have large impacts on O_3 concentrations.

Previous global and regional modeling studies have shown that aerosols influence O_3 concentrations in China by heterogeneous reactions. Liao and Seinfeld (2005) found that simulated surface-layer O_3 concentrations over eastern China can be reduced by 25–30% due to heterogeneous reactions on sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), sea salt, and mineral dust aerosols, accounting for the hydrolysis of N_2O_5, irreversible absorption of NO_3, NO_2, and HO_2 on wetted aerosol surfaces, mineral dust uptake of SO_2, O_3, and HNO_3, as well as the sea salt uptake of SO_2 in a coupled global chemistry–aerosol–climate model based on the Goddard Institute for Space Studies (GISS) GCM II' at 4°×5° resolution. Tie et al. (2005) used a coupled global aerosol–chemistry model, Model for Ozone and Related Chemical Tracers (MOZART) with a horizontal resolution of 2.8°×2.8°, to study the impacts of heterogeneous reactions on O_3 by considering the heterogeneous reactions of HO_2 and CH_2O on sulfate aerosol as well as the uptake of O_3 on black carbon (BC). They found that O_3 concentrations were reduced by 10–15% and 5–10% in eastern China in winter and summer, respectively. Pozzoli et al. (2008) showed that surface-layer O_3 concentrations were reduced by 18–23% over the Transport and Chemical Evolution over the Pacific (TRACE-P) region in March of 2001, when all the heterogeneous reactions listed in Liao and Seinfeld (2005) were considered in the coupled ECHAM5-HAMMOZ model with a spatial resolution of 2.8°×2.8°. Xu et al. (2012) used the Community Multi-scale Air Quality Model (CMAQ) with a horizontal resolution of 4 km to study the impacts of heterogeneous reactions on O_3 during a high O_3 episode occurred in Beijing in June 26–27, 2000. They reported that the impacts of heterogeneous reactions on O_3 depend on the local NO_x/VOC ratio. For example, the absorption of NO_2 by aerosols was found to increase O_3 at noon by 4–20 ppbv (or 3–14%) in VOC-limited urban areas and to decrease O_3 by 4–10 ppbv (or 3–7%) in NO_x-limited sub-urban areas.

Previous modeling studies have also shown that aerosols can influence O_3 in China by altering photolysis rates. Tang et al. (2004) found that O_3 concentrations were reduced by 0.1–0.8% in northeastern China during the dust event of April 4–14, 2001, by using the Sulfur Transport and Emissions Model (STEM) with a spatial resolution of 80 km, as a result of the dust-induced changes in photolysis rates. Tie et al. (2005) showed that surface-layer photolysis rates $J(O_3)$ and $J(NO_2)$ in eastern China were reduced, respectively, by 20–30% and 10–30% in winter as well as 5–20% and 1–10% in summer, leading to reductions in surface-layer O_3 concentrations by 2–4% in winter and less than 2% in summer. Li et al. (2011) used a regional Nested Air Quality Prediction Model System (NAQPMS) with a horizontal resolution of 81 km to estimate the changes in photolysis rates in central eastern China by SO_4^{2-}, NO_3^-, NH_4^+, OC, BC, and mineral dust aerosols during June 1–12, 2006. They reported that aerosols reduced daytime average $J(O^1D)$ in layers below 1 km, 1–3 km, and 3–10 km by 53.3%, 37.2%, and 20.9%, respectively, which led to changes in O_3 concentrations by −5.4%, −3.8% and 0.1% in those three layers, respectively.

Few previous studies examined the combined impacts of aerosols on O_3 by both heterogeneous reactions and aerosol-induced changes in photolysis rates. Martin et al. (2003) considered the heterogeneous reactions of HO_2, NO_2, NO_3, and N_2O_5 as well as the optical properties of SO_4^{2-}, BC, OC, sea salt, and mineral dust in the global three-dimensional Goddard Earth Observing System chemical transport model (GEOS-Chem) at 2°×2.5° resolution, and found that O_3 concentrations were reduced by 5–10 ppbv (10–15%) over northeastern China in March and by up to 5 ppbv over North China Plain in August of 1997. This study, however, excluded the impacts of hydrolysis of N_2O_5, did not consider NO_3^- and NH_4^+ aerosols in the calculation of photolysis rates, and did not examine the spatial and temporal variations of the impacts of aerosols on O_3 concentrations in China.

The studies cited above underscored the important impacts of aerosols on tropospheric O_3 in China. The goal of this study is to examine systematically the impacts of aerosols on O_3 concentrations in China using the nested-grid version of the GEOS-Chem model with a horizontal resolution of 0.5° latitude by 0.667° longitude driven by the assimilated meteorological fields. We pay special attention to (1) the spatial and temporal variations of the impacts of aerosols on O_3, and (2) the role of each and all heterogeneous reactions. We focus especially on the impacts in four heavily polluted regions in China, including Beijing–Tianjin–Tanggu (BTT, 35°–40°N, 114°–120°E), Yangtze River Delta (YRD, 29.5°–32.5°N, 118°–122°E), Pearl River Delta (PRD, 21°–23.5°N, 112–116°E), and Sichuan Basin (SCB, 28°–31.5°N, 102.5°–107.5°E).

The description of model and numerical experiments is presented in Section 2. Simulated concentrations aerosols and O_3 are presented and evaluated in Section 3. Sections 4 and 5 examine, respectively, the impacts of aerosols on concentrations of O_3 by heterogeneous reactions alone and by changes in photolysis rates alone. The combined effects are presented in Section 6 and the associated model uncertainties are discussed in Section 7.

2. Model description

2.1. GEOS-Chem model

We simulate concentrations of O_3 and aerosols using the one-way nested-grid capability of the global chemical transport model GEOS-Chem (version 9.1.2, http://acmg.seas.harvard.edu/geos/). GEOS-Chem is driven by the GEOS-5 assimilated meteorological fields from the Goddard Earth Observing System of the NASA Global Modeling Assimilation Office. The nested domain for Asia (70–150°E, 10°S–55°N) has a horizontal resolution of 0.5° latitude by 0.667° longitude and 47 vertical layers up to 0.01 hPa. Tracer concentrations at the lateral boundaries are provided by a global GEOS-Chem simulation at 4° latitude by 5° longitude horizontal resolution and updated in the nested-grid model every 3 h (Chen et al., 2009).

The GEOS-Chem model has fully coupled O_3–NO_x–hydrocarbon chemistry and aerosols including $SO_4^{2-}/NO_3^-/NH_4^+$ (Park et al., 2004; Pye et al., 2009), OC and BC (Park et al., 2003), sea salt (Alexander et al., 2005), and mineral dust (Fairlie et al., 2007). Tropospheric O_3 is simulated with about 80 species and over 300 chemical reactions (Bey et al., 2001). Partitioning of nitric acid and ammonia between the gas and aerosol phases is calculated by ISORROPIA II (Fountoukis and Nenes, 2007). SOA formation considers the oxidation of isoprene (Henze and Seinfeld, 2006), monoterpenes and other reactive VOCs (ORVOCs) (Liao et al., 2007), and aromatics (Henze et al., 2008). The mineral dust and sea salt aerosols are not considered in this study.

2.2. Heterogeneous reactions on aerosols

Heterogeneous reactions on anthropogenic aerosols in the GEOS-Chem model are listed in Table 1, including hydrolysis of N_2O_5 (Evans and Jacob, 2005), irreversible absorption of NO_3 and NO_2 on wet aerosols (Jacob, 2000), and the uptake of HO_2 by