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Inorganic aerosols responses to emission changes in Yangtze River Delta, China

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HIGHLIGHTS

- Inorganic aerosols' seasonality and contribution for $PM_{2.5}$ are examined over YRD.
- Nighttime hydrolysis of N_2O_5 was demonstrated to be responsible for nitrate enhancement over YRD for all seasons.
- Nitrate mass concentration might be increased under NOx emission reduction in winter over YRD.

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ABSTRACT

The new Chinese National Ambient Air Quality standards (CH-NAAQS) published on Feb. 29th, 2012 listed $PM_{2.5}$ as criteria pollutant for the very first time. In order to probe into $PM_{2.5}$ pollution over Yangtze River Delta, the integrated MM5/CMAQ modeling system is applied for a full year simulation to examine the $PM_{2.5}$ concentration and seasonality, and also the inorganic aerosols responses to precursor emission changes. Total $PM_{2.5}$ concentration over YRD was found to have strong seasonal variation with higher values in winter months (up to 89.9 μg/m^3 in January) and lower values in summer months (down to 28.8 μg/m^3 in July). Inorganic aerosols were found to have substantial contribution to $PM_{2.5}$ over YRD, ranging from 37.1% in November to 52.8% in May. Nocturnal production of nitrate (NO_3^-) through heterogeneous hydrolysis of N_2O_5 was found significantly contribute to high NO_3^- concentration throughout the year. In winter, NO_3^- was found to increase under nitrogen oxides (NOx) emission reduction due to higher production of N_2O_5 from the excessive ozone (O_3) introduced by attenuated titration, which further lead to increase of ammonium (NH_4^+) and sulfate (SO_4^{2-}), while other seasons showed decrease response of NO_3^-. Sensitivity responses of NO_3^- under anthropogenic VOC emission reduction was examined and demonstrated that in urban areas over YRD, NO_3^- formation was actually more sensitive to VOC than NOx due to the O_3-involved nighttime chemistry of N_2O_5, while a reduction of NOx emission may have counter-intuitive effect by increasing concentrations of inorganic aerosols.

1. Introduction

Fine aerosols ($PM_{2.5}$) has been listed as one of the criteria air pollutants in National Ambient Air Quality Standard (NAAQS) and thoroughly investigated in United States due to its adverse effects on public health, reduction of visibility, and also climate forcing in the past decade. Although the knowledge about $PM_{2.5}$ in China is limited due to relative less emphasis (Chan and Yao, 2008), the necessity of understanding $PM_{2.5}$ is well recognized recently. On Feb. 29, 2012, The Chinese Ministry of Environmental Protection (MEP) published the new China National Ambient Air Quality Standard (CH-NAAQS) in which $PM_{2.5}$ was announced as criteria pollutant for the very first time. Although both the annual (35 μg/m^3) and daily (75 μg/m^3) standards configured within CH-NAAQS are less strict compared with the US-NAAQS (15 μg/m^3 and 35 μg/m^3 for annual and daily standard, respectively), the significantly increased news reports about $PM_{2.5}$ thereafter implied the strong public interest in this issue. Especially, the national wide haze engulfed a large portion of Eastern China during the past winter promoted the important urgency for more efforts dedicated to understand $PM_{2.5}$ pollution. China National Environmental Monitoring Centre (CNEMC) reported monitored monthly average $PM_{2.5}$ for 74 major cities was 130 μg/m^3 and 85 μg/m^3 for January and February 2013, respectively (CNEMC, 2013), while the observed maximum daily average values were 766 μg/m^3 and 232 μg/m^3 for the two months, which substantially exceeded the CH-NAAQS.

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Several pilot studies have already been performed with observational or modeling method to probe into $PM_{2.5}$ pollution over China from different perspectives. Streets et al. (2007) assessed local anthropogenic emission contribution to particles formation and reported observed daily average $PM_{2.5}$ ranged from 75 to 145 μg/m^3 in Beijing; Fu et al. (2010) examined pollution event driven by dust storm in Shanghai based on observations and reported 383 μg/m^3 $PM_{2.5}$ in April 2007; Fu et al. (2012b) investigated biomass burning impacts from southeast Asia with modeling method and reported long-range transport could contribute to 64 μg/m^3 over Eastern Asia. A couple of pioneering studies conducted recently also provide more detailed information about $PM_{2.5}$ speciation over China. Huang et al. (2012) examined the composition measurements of $PM_{2.5}$ in Shanghai, and reported inorganic aerosols (nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+)) could contribute up to 77% (48.86 ± 5.01 μg/m^3) of total $PM_{2.5}$ in typical pollution episodes, of which nitrate/sulfate ratio was also found to increase from 0.43 in 2000 to 0.75 in 2009. Pathak et al. (2011) reported observed exceptionally high concentrations of nitrate up to 42 μg/m^3 in Beijing and Shanghai, and concluded the high level summer time nitrate was due to hydrolysis of N_2O_5 based on box model simulation. Zhao et al. (2013a,b) reviewed the impacts of anthropogenic emission changes in China and reported up to 4.22 μg/m^3 of $PM_{2.5}$ deduction due to NOx and SO_2 emission reduction.

The above studies mainly focused on special air pollution episodes, while few of them have been performed to provide comprehensive examination of $PM_{2.5}$ pollution regarding its formation schemes, seasonality, and spatial distribution over China. Although studies applying box model described the essential inorganic aerosol chemistry mechanism, it can only represent some domain-averaged chemistry instead of distinguishing different chemical regimes. Fundamental uncertainties still exist due to the essential assumptions employed by box model such as stagnant conditions and aloft carry-over of air pollutants. Pathak et al. (2011) assumed a fixed ratio for NO_2/NOy and a linear relationship between nitric acid (HNO_3) and nitrogen dioxide (NO_2) to predict nitrate formation, while a steady-state might hardly be reached with intensive emission and rapid convection. More importantly, only a few studies have been documented to examine $PM_{2.5}$ responses to precursor emission changes over China. So in this paper, we applied MM5/CMAQ modeling system for a full year simulation to examine the seasonal variations of $PM_{2.5}$ over Yangtze River Delta (YRD). Anthropogenic emission control scenarios were also employed to investigate the sensitivity responses of inorganic aerosols to precursor emission changes. YRD was selected as the research area because it is one of the most important commercial and industrial center within China, and also a highly populated region with more than 80 million residences, of which 50 million are urban. Model description and evaluation was provided in Section 2. Section 3 discussed the seasonality of $PM_{2.5}$, and the inorganic aerosol responses in different seasons under predefined NOx and VOC emission control scenarios. Section 4 draws conclusions and summarizes major challenges and future prospects.

2. Materials and methods

2.1. Model description and simulation design

Community Multiscale Air Quality (CMAQ) modeling system developed by the US EPA (Byun and Schere, 2006) was selected to conduct simulations in this study. CMAQ has been widely applied to predict air pollutions over China in different studies and demonstrated its reliability (Fu et al., 2012b, 2013; Streets et al., 2007; Wang et al., 2014). In this study, CMAQ v4.6 was configured with 19 vertical layers extending from ground surface to 100mb with denser layers in lower atmosphere to better represent the mixing layer. There were three one-way nested modeling domains D1, D2, and D3 which mainly covered East Asia, eastern China, and YRD respectively, as shown in Fig. 1 (detailed model configuration is summarized in Table S1). We mainly focused on domain D3 which covered Shanghai, southern Jiangsu province and northern Zhejiang province with a 3 × 3 km grid resolution. Initial and boundary conditions for domain D1 was generated from GEOS-Chem global modeling results following the algorithm described in Lam and Fu (2009). Shanghai was selected as a representative city in this study to assess $PM_{2.5}$ pollution in typical urban areas within YRD. The meteorology filed was generated by the fifth-generation the National Center for Atmospheric Research (NCAR)/Penn State Mesoscale Model (MM5 version 3.3). Anthropogenic emission inputs for CMAQ modeling system was provided by the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) 2006 emission inventory (Zhang et al., 2009). Species include sulfur dioxide (SO_2), nitrogen oxides (NOx), carbon monoxide (CO), non-methane volatile organic compounds (NMVOC), PM_{10}, $PM_{2.5}$, black carbon aerosol (BC), organic carbon aerosol (OC), ammonia (NH_3), and methane (CH_4). NMVOC was categorized into 16 subspecies to match the CB05 chemical mechanism utilized in CMAQ (Yarwood et al., 2005). The 2D grid-cell emissions were obtained using top-down method (Du, 2008). Biogenic emissions were generated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012).

Besides the baseline simulation, emission control simulations were also conducted in order to understand the sensitivity responses of

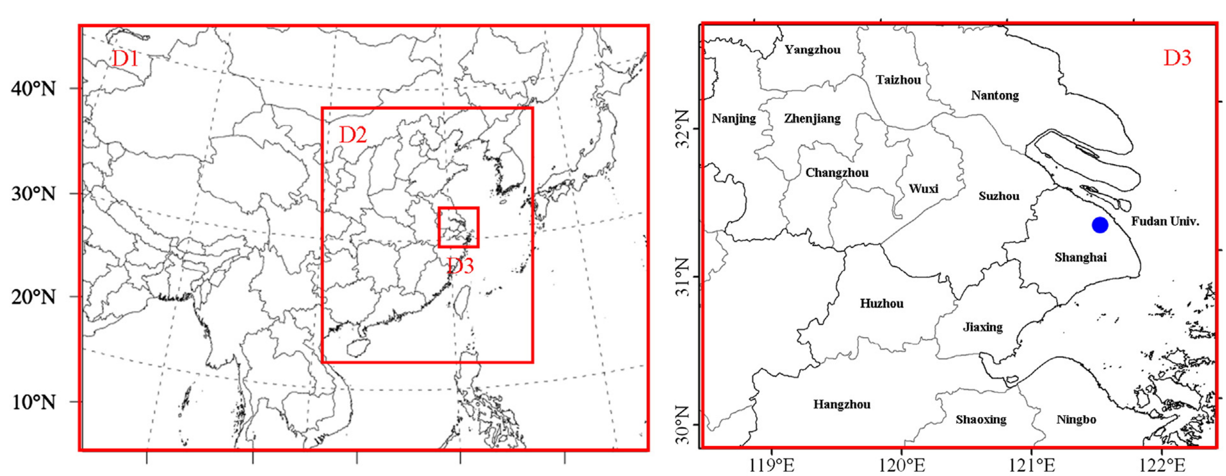

Fig. 1. Three one-way nested modeling domains at 27-km (East Asia: D1), 9-km (East China: D2), and 3-km (Yangtze River Delta: D3) resolutions. Blue cycle represents the observation site Fudan University. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)