



Chemical competition in nitrate and sulfate formations and its effect on air quality



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HIGHLIGHTS

- Chemical competition in nitrate and sulfate formations is significant for air quality.
- It alters the relationship between nitrate and its precursor emissions.
- It raises the nitrate level even reducing precursor emissions under the A1B scenario.
- It may upset the expected improvement in visibility by emission reduction.
- The competition will increase the difficulty in air quality planning and mitigation.

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ABSTRACT

The competition for bases in nitrate and sulfate aerosol formations significantly affects the concentration of nitrate aerosols. Sensitivity experiments with reduced sulfate precursor emissions, achieved through the use of the CAM-Chem model, show that nitrate concentration is particularly affected by sulfate precursor emissions in winter when their changes are linearly correlated. As a result, the nitrate concentration in the atmosphere is less affected by its own precursor emissions. The concentration-precursor emission relationship for sulfate is not significantly affected by the competition. The future air quality projection following the IPCC A1B emission change scenario shows that the decrease in sulfate precursor emissions and increase in ammonia emissions by 2050 will lead to adverse changes in nitrate concentrations. This will be in response to the reduction in its precursor emissions over the major industrial region of the United States. Due to the difference between nitrate and sulfate aerosols in physical properties and efficiency in cloud condensation, the visibility reduction caused by sulfate emission control occurs over industrial regions in winter. The resulting adverse changes in visibility to emission control will further increase the uncertainty in assessing air quality change. The nonlinear relationship between precursor emissions and changes in pollution levels will increase the difficulty in making effective air quality control strategies.

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1. Introduction

Nitrate (NO_3^-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) are important constituents of particulate matter (PM). They may seriously affect human health and reduce visibility [Watson, 2002]. As secondary inorganic aerosols (SIA), they form mainly from gas-phase precursors which are mostly industrial emissions. SIAs have been listed as the major pollutants in air quality standards [EPA, 2008], and the direct strategy to reduce the level of SIA is to

control industrial emissions of precursors. This may be an effective method overall to reduce pollution, but it may not work for nitrate aerosols. Future projections of global sulfate-ammonium-nitrate levels (under the IPCC AIFI, A1B and B1 scenarios) show that changes in nitrate aerosol levels do not follow a linear relationship with changes in precursor emissions [Liang et al., 2009]. Some opposite relationships between concentration and precursor emissions are also found (e.g., nitrate increases in response to emission reduction) [Pye et al., 2009].

A hypothesis to explain these results is that the nitrate aerosol level is not only determined by its precursor emission, but also affected by the availability of sulfate aerosol precursors. In the aerosol production stage, nitrate and sulfate aerosols are connected by the participation of bases (mainly ammonia (NH_3)) [Stelson

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Table 1
Major chemical reactions in the formation of nitrate-sulfate aerosols [Seinfeld and Pandis, 1998].

Reactions	Environment & type
1. $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{HO}$	Gaseous
2. $\text{NO}_2 + \text{HO} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	Gaseous
3. $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	Gaseous
4. $\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	Gaseous
5. $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	Gaseous, aqueous
6. $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$	Gaseous
7. $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$	Gaseous
8. $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	Gaseous
9. $\text{SO}_2 \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O}$	Gaseous, aqueous
10. $\text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+$	Aqueous
11. $\text{HSO}_3^- + \text{H}_2\text{O}_2 \leftrightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{H}_2\text{O}$	Aqueous
12. $2\text{NH}_3 + \text{H}_2\text{SO}_4 \leftrightarrow (\text{NH}_4)_2\text{SO}_4$	Heterogeneous (gas-aqueous/solid)
13. $\text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$	Heterogeneous (gas-aqueous/solid)

et al., 1983]. The environmental factors that play an important role in their formation include moisture, temperature, pressure, and wind speed [Seinfeld and Pandis, 1998]. Although the formation processes are very complex, the relationship between precursors and products are conserved under the view of mass transfer. Major chemical processes linking precursors and aerosols are acid–base reactions of acid precursors in the presence of base, and ammonia is the main base precursor [Aw and Kleeman, 2003; Liao et al., 2006; Dawson et al., 2007; Rae et al., 2007]. However, in the real atmosphere, the base concentration usually is not abundant enough to react with all acid precursors. Therefore, nitrate and sulfate precursors are likely to “compete” for ammonia. Under ambient atmospheric conditions, environment factors including temperature, humidity, and wind speed affect the physical and chemical processes in this competition. Ammonium-sulfate is relatively easier to form than ammonium-nitrate [Seinfeld and Pandis, 1998]. The amount of available ammonia for the formation of ammonium nitrate is affected by the consumption in sulfate production. As a result, projections of future aerosol level change under different scenarios cannot be linearly associated with precursor emissions.

In this study, we examine the competition between nitrate and sulfate formations, and its impact on air quality. The emission inventory for 2000 from the Precursors of Ozone and their Effects in the Troposphere (POET) database is employed here as the standard inventory [Granier et al., 2005]. By modifying the standard emissions, a series of sensitivity experiments using the Community Atmospheric Model with Chemistry (CAM-Chem) version 4 [Lamarque et al., 2012] are implemented to analyze the possible linkage between the changes in nitrate and sulfate aerosols. A projection of emissions in 2050, following the IPCC A1B climate and emission change scenarios, is employed to assess the effect of this chemical competition on future air quality. The influence on pollutant concentrations and visibility are analyzed.

2. Method

The formation mechanisms for sulfate and nitrate aerosols are very complicated, and involve a series of homogeneous and heterogeneous processes. The environmental vapor pressure and temperature are sensitive factors in affecting the equilibriums. However, for fixed environmental conditions, changes in precursor emissions due to human activities would be the main factor in affecting aerosol formations. Major chemical reactions associated with nitrate and sulfate formations are shown in Table 1, which includes the gaseous, aqueous and some heterogeneous processes (gas-to-aqueous; gas-to-solid). These reactions have been widely used in determining whether the formation of aerosols occurs in

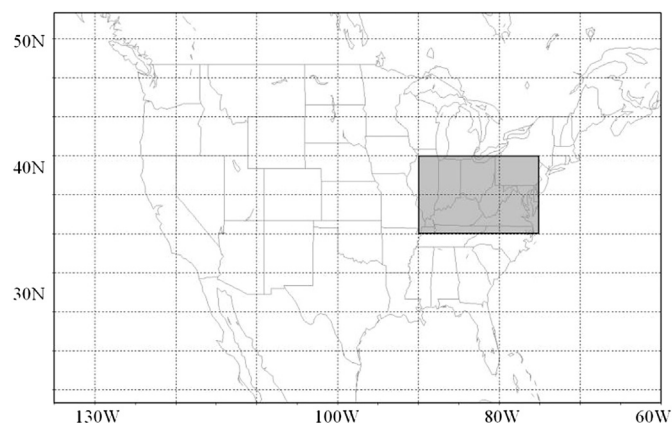


Fig. 1. The shaded rectangle region is the sensitivity region used for analysis. The area is within latitude 36°N–42°N; longitude 90°W–75°W.

the solid or aqueous phase [Schwartz, 1981; Seinfeld and Pandis, 1998; Blanchard and Hidy, 2003]. Due to the advantages in chemical kinetics and thermodynamic equilibrium, ammonium-sulfate formations are preferred in a mixing environment including nitrate precursors [Kim et al., 1993a, 1993b; Seinfeld and Pandis, 1998; Blanchard and Hidy, 2003]. This priority may result in both sulfate and nitrate precursors competing for ammonia, which is usually limited in the atmosphere [Blanchard et al., 2000]. In addition, the formation of nitrate and sulfate aerosols is also affected by environmental factors including temperature, humidity, and solar radiation [Seinfeld and Pandis, 1998; Chang et al., 2009]. Therefore, the competition becomes complicated and the resulting effect on nitrate aerosol concentrations can be very significant.

For the numerical simulations in this study we use the CAM-Chem climate chemistry model [Heald et al., 2008; Pfister et al., 2008; Lamarque et al., 2012; Lei et al., 2012, 2013], which is a part of the Community Earth System Model (CESM) and is based on the chemical component of the Model of Ozone and Related Chemical Tracers (MOZART) [Emmons et al., 2010]. The chemical module includes 85 gas-phase species, 12 bulk aerosol compounds, 39 photolysis, and 157 gas-phase reactions. The aerosol module considers sulfate, black carbon, primary organic, secondary organic, ammonium nitrate, and sea salt [Lamarque et al., 2012]. From the viewpoint of air quality, the significant improvements in CAM-Chem over MOZART are to better consider the aerosol processes and to incorporate dynamic modules for interactions with meteorological and biogenic processes [Guenther, 1997; Horowitz et al., 2003; Lamarque et al., 2012]. In simulations of secondary inorganic aerosol concentrations, the CAM-Chem model includes necessary homogeneous and heterogeneous processes that represent the latest understanding on aerosol dynamics [Metzger et al., 2002; Lamarque et al., 2012]. The simulations of sulfate and nitrate aerosol concentrations have been validated in comparison with observations [Lamarque et al., 2012]. When fully coupled with radiation and cloud modules, CAM-Chem can also calculate the direct and indirect effects of aerosols based on the aerosol optical depth and composition [Lamarque et al., 2012].

In order to examine the effect of competition between nitrate and sulfate on nitrate particle concentrations, a series of sensitivity experiments are designed to test the sensitivity of aerosol levels to sulfate precursor emission changes. These experiments include three runs with a 50% reduction, an 80% reduction, and a 90% reduction in SO_x emissions, respectively. Since the chemical competition is supposed to be sensitive in industrial regions, a sensitivity area in the industrial region of the eastern United States is defined to analyze the changes in aerosol levels. Detailed

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