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Aerosols in an arid environment: The role of aerosol water content, particulate acidity, precursors, and relative humidity on secondary inorganic aerosols

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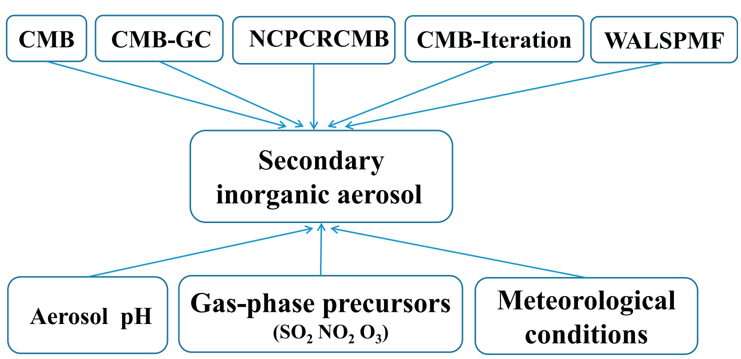
HIGHLIGHTS

- Secondary aerosol in Hohhot was low.
- Aerosol pH was estimated by a thermodynamic equilibrium model.
- Multiple receptor models were used to explore the source contributions.
- Aerosol water content and particulate acidity were positively associated with secondary SO_4^{2-}.
- NO_2 and RH had a significant impact on secondary NO_3^- in an arid atmosphere.

GRAPHICAL ABSTRACT



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ABSTRACT

Meteorological conditions, gas-phase precursors, and aerosol acidity (pH) can influence the formation of secondary inorganic aerosols (SIA) in fine particulate matter ($PM_{2.5}$). Most works related to the influence of pH and gas-phase precursors on SIA have been laboratory research, but field observation research is very scarce, especially in arid environments. The relationship among SIA, pH, gas-phase precursors, and meteorological conditions are investigated in Hohhot, a major city in China with an arid environment. Secondary inorganic species, e.g., SO_4^{2-}, NO_3^-, were typically found at low levels, reflecting the low level of secondary aerosol. It is interesting to note that the level of SO_2 in Hohhot was higher than in other cities while SO_4^{2-} was relatively lower than in other cities. Multiple receptor models were used to explore the contributions to the SIA and quantify the source impacts on the SIA. Annual average aerosol pH in Hohhot was 5.6 (range 1.1–8.4) which was estimated by a thermodynamic equilibrium model. Additionally, a statistical method was used to evaluate the influence of SIA sources on ambient aerosol concentrations. Aerosol water content and particulate acidity were found to be positively associated with secondary SO_4^{2-}, while NO_2 and RH had a significant impact on secondary NO_3^- in an arid atmosphere. The

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findings explain the relationship between gaseous precursors, relative humidity, aerosol pH and temperature in the arid city of Hohhot.

1. Introduction

With the rapid industrialization and urbanization in China and abroad, air quality is declining rapidly around the world which has made research on atmospheric aerosols important increasingly. Atmospheric aerosols can be classified into two types: primary aerosol and secondary aerosol (Chowdhury et al., 2007). Primary aerosols are emitted from various anthropogenic and natural sources directly such as vehicle exhaust, coal combustion, crustal dust, and cement. Secondary aerosols, are formed through gas-to-particle transformation processes and oxidizing reactions, such as a sulfate or nitrate (Xue et al., 2016; Jaiprakash et al., 2017). High particulate matter (PM) levels and haze events are dominated by secondary inorganic aerosol (SIA) pollution (Mysliwiec and Kleeman, 2002; Wang et al., 2014a, 2014b), which is produced from gas-phase precursors, especially sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) (Huang et al., 2010; Zhang et al., 2013). SIA have a strong effect on the hygroscopicity and acidity of aerosols which could influence aerosol-phase chemistry and the uptake of gas-phase species by particles (Xue et al., 2011; Shon et al., 2012). In the formation of SIA meteorological conditions (temperature, wind speed, and humidity) and gas-phase precursors were important factors (Pun and Seigneur, 2001; Wang et al., 2015; Han et al., 2016). Wang et al. (2014a, 2014b) concluded that during the haze episodes in the Jing-Jin-Ji area, sustained weak wind, growing humidity, and continuously high humidity conditions were the leading meteorological causes for severe pollution levels. Temperature was connected to the rates of the SO_2 oxidation and the formation of secondary sulfate (Ronneau, 1987; Seinfeld and Pandis, 2006). Temperature also affects the partitioning of nitrate (NO_3^-) in the atmospheric fine and coarse fraction of aerosols (Wakamatsu et al., 1996; Han et al., 2016). Higher humidity can create favorable conditions for aqueous reactions and lead to the formation of SIA (Han et al., 2016). Moreover, during higher relative humidity (RH) conditions, nitric acid (HNO_3) and ammonia (NH_3) can be dissolved, and particulate NO_3^- and ammonium (NH_4^+) formation may accelerate (Trebs et al., 2004, 2005; Han et al., 2016). Furthermore, SO_2, NO_2, and O_3 are precursors of SIA, and these precursors have close relationships with the formation of SIA (Pun and Seigneur, 2001; Amil et al., 2016).

Cheng et al. (2016) showed that in the relative alkaline condition in Beijing, nitrogen may promote the secondary sulfate formation including field observation and modelling study. Tie et al. (2017) investigated the positive feedback loop between SIA and meteorology. However, the SIA studies focused on the arid regions in China, Hohhot was rare. As the typical arid region in China (the annual RH was <50%), the geographic location of Hohhot (the capital and center of Inner Mongolia) was specific, the Köppen climate classification for Hohhot is also cold semi-arid climate, the pollution source characteristics, the RH, the dust period in Hohhot were different from Beijing and other northern regions, the level of SIA formation can be very different compared to other regions. So it is essential to explore the level of SIA, the influence of meteorological conditions and precursors on SIA in Hohhot.

To further address the relation among pH, gaseous precursors, and meteorological conditions of secondary sulfate, the level of secondary aerosol should be analyzed first. Receptor models are commonly used to apportion the contribution of SIA. For aerosol pH, because it is difficult to measure directly (Song et al., 2018), a thermodynamic equilibrium model (ISORROPIA-II) was used to predict pH in this study. ISORROPIA-II was also used to estimate other characteristics of aerosol such as water content. Here three items were investigated. First, 1) concentrations of $PM_{2.5}$, which represented the four different seasons, were obtained by the offline filter sampling, and the corresponding meteorological conditions and levels of gas-phase pollutants (WS, RH, T, NO_2, SO_2, O_3) in Hohhot were also acquired. Next, 2) aerosol pH was investigated using ISORROPIA-II, and receptor models were used for source identification. Finally, 3) statistical methods were employed to analyze the relative influence of meteorological conditions, gas-phase precursors, and aerosol pH on the SIA to understand the formation of SIA in Hohhot. The findings in this work can provide useful information regarding formation mechanisms of SIA in arid environments.

2. Materials and methods

2.1. Study area

Hohhot, an arid city located in central Inner Mongolia, northern China, has typical continental climate with high winds and little rain in spring (Fig. S1). The diurnal maximum wind speed can typically about 10 m/s which may result in periods of high wind-blown dust. The annual precipitation is 390 mm, with most of the precipitation occurring in July and August, and this is much lower than the annual evaporation capacity of 2000 mm, so the ground is typically dry. High winds contribute to the arid environment. The power industry accounts for a majority of the total coal consumption in Hohhot. The heating period in Hohhot begins in mid-October and ends around mid-April the following year.

2.2. ISORROPIA II

ISORROPIA-II is a thermodynamic equilibrium model that predicts equilibrium partitioning of species (Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-) between the gas and particle phases using measured particulate species to evaluate fine particle pH levels (Tian et al., 2013a, 2013b). Model inputs include gas and particle concentrations of species that affect the value of pH (Fang et al., 2017). In this study, ISORROPIA-II was run in the forward mode and "metastable" phase state, but NH_3 was not included. Further information about ISORROPIA-II can be obtained in other studies (Guo et al., 2015, 2016; Weber et al., 2016).

2.3. Meteorological parameters, gas-phase pollutants, and air mass back trajectories

The datasets of meteorological parameters and gas-phase pollutants were obtained online using https://www.wunderground.com/ and http://www.aqistudy.cn/, respectively, to identify the seasonal variations of meteorological parameters and gas-phase pollutants during the sampling period in Hohhot. The analysis of air mass back trajectories was dependent on the TrajStat, a geographic information system (GIS) software that uses various trajectory statistical analysis methods to identify potential aerosol sources from long-term air pollution measurement data (http://www.meteothinker.com/Downloads.html). The meteorological data used in this model was downloaded at http://www.arl.noaa.gov/HYSPLIT.php (including horizontal and vertical wind speed, temperature, pressure, relative humidity, precipitation, etc.). In this study, two-day air mass back trajectories were calculated every 6 h using the TrajStat model initiated at 1000 m above ground level, located at 111.41° east longitude and 40.48° north latitude (the center of Hohhot). The related analysis by TrajStat model can be seen in the Supplementary Information.