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Evolution of particulate sulfate and nitrate along the Asian dust pathway: Secondary transformation and primary pollutants via long-range transport

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ABSTRACT

Both $PM_{2.5}$ and TSP over Yulin, a rural site near the Asian dust source region, were collected from 2007 to 2009. Characteristics, sources, and formation mechanisms of sulfate and nitrate were investigated. SO_4^{2-} displayed a distinct seasonal variation with the highest average concentration observed in summer when SO_4^{2-} accounted for an average of 14.1% and 13.7% of the $PM_{2.5}$ and PM_{coarse} mass concentrations, respectively. Ambient temperature and relative humidity were two important factors influencing the formation processes of SO_4^{2-} and NO_3^-. In summer, the high concentrations of SO_4^{2-} in $PM_{2.5}$ were probably from the gas phase oxidation of SO_2, while the low concentrations of NO_3^- in $PM_{2.5}$ were attributed to the high temperature that was not favorable for the formation of NH_4NO_3. In spring, autumn, and winter, SO_4^{2-} and NO_3^- were significantly enhanced in those days with high relative humidity, implying that in-cloud/aqueous processing dominated the formations of SO_4^{2-} and NO_3^-. Different from $PM_{2.5}$ in which NH_4^+ acted as the dominant neutralizer for acids, alkaline species such as Ca^{2+} and Mg^{2+} played an important role in the formation of sulfate and nitrate salts in coarse particles throughout the whole year. During the dust event days, SO_4^{2-} in coarse particles significantly increased, while black carbon and NO_3^- largely decreased, suggesting that the primary mineral dust could be one of the major sources of SO_4^{2-}. By comparing the mass ratio of $SO_4^{2-}/3/S$ in the dust aerosols of Yulin with different dust source regions (i.e., Taklimakan Desert and Gobi Desert) and the application of air mass backward trajectory analysis, it was found the long-range transported dust from the Taklimakan Desert, which was rich in primary sulfate due to its paleo-ocean characteristics, was a non-negligible source of SO_4^{2-} over Yulin. In spring and winter, the prevailing northerlies and northwesterlies promoted chemical interaction between alkaline mineral dust and acid gaseous precursors from local and/or regional emissions. While in summer, regional transport facilitated by the southerlies and southeasterlies may contribute to the high secondary aerosol concentrations over Yulin. This study demonstrated that a considerable portion of aerosol over a Chinese rural area could be derived from complex chemical reactions via long-range/regional transport.

1. Introduction

Asian dust and its transport have great impacts on regional air quality (e.g., Fu et al., 2008; Zhao et al., 2011) as it carries not only mineral aerosols but also pollution matter to the atmosphere over the downwind regions. During the transport, mineral aerosols can mix and interact with anthropogenic pollutants, leading to a significant increase of pollution matters, such as sulfate and nitrate (Manktelow et al., 2010; Usher et al., 2002; Zhang et al., 2000). The formation of sulfate and nitrate on mineral particles influences the hydrophilicity of the particles (Shi et al., 2008), which in turn can impact the further chemical reactions on the particles. The modification of dust aerosol during the transport can cause high uncertainties in evaluating its environmental effects.

Sulfate is of great concern for its effect on climate change (IPCC, 2007), and its role in atmospheric chemical and physical processes (Sipila et al., 2010; Yue et al., 2010). Nitrate is now attracting more and more attention, as NO_X emission has been increasing across China over the past decade (Guinot et al., 2007; Streets et al., 2003; Zhang et al., 2007). As both sulfate and nitrate are two major water-soluble ions in aerosols, the high emissions of SO_2 and NO_X, their transformations to

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sulfate and nitrate, and their long/medium-range transport would have significant impact on the air quality of the downwind regions.

China is now a hot spot region for air pollution and global climate change studies (Chang et al., 2010; Morino et al., 2011). Intensive studies were designed to investigate the sources and formation mechanisms of particulate sulfate and nitrate over China (e.g., Guo et al., 2010a; Xiao et al., 2009; Yao et al., 2002). However, most studies focused on big urban cities, while relatively few studies were conducted for remote areas nearby the dust sources, where the interaction between the natural mineral dust and anthropogenic emissions were most active. Yulin, the sampling site in this study, is located at the northern edge of the Chinese Loess Plateau and on the transport pathway of Asian dust from northern and northwestern China to the North Pacific (Zhang et al., 2008). It is also in the depositional region of the dust from both the Taklimakan Desert (Liu et al., 1994) and Gobi Desert (Sun et al., 2001). In addition, Yulin is surrounded by a number of big coal mines with intensive industrial activities. In this regard, Yulin could be treated as a good representative site for investigating aerosols from complex sources. In this study, a multi-year sampling of aerosol was conducted at Yulin, and the characteristics and sources of sulfate and nitrate were probed. Specifically, different formation mechanisms of secondary aerosol were studies on a seasonal basis.

2. Methods

2.1. Study site and field sampling

Both $PM_{2.5}$ (particle size smaller than 2.5 μm) and TSP (total suspended particles) were collected in Yulin (YL), Shaanxi province of China, and its location is shown in Fig. 1. YL is the northernmost prefecture-level city of Shaanxi province and lies in the transition zone between the Loess Plateau and deserts. As shown in Fig. 1, to the north and northwest of the city it is the Ordos Desert (also known as Mu Us Desert) of Inner Mongolia. YL is characterized of a continental, monsoon-influenced semi-arid climate. The definition of the four seasons in this study is from March to May for spring, June to August for summer, September to November for autumn, and December to February for winter, respectively, with each season encompassing the entirety of the included months. In winter, it is very cold with rather long durations, while in summer, it is hot and somewhat humid. Desertification due to wind erosion has been severe in this region. Aerosol samples were collected from 2007 to 2009 to study the characteristics of mineral and pollution aerosol over the areas nearby dust sources. The samplers were set up about 10 m above the ground. Aerosol sampling in 2007 was conducted from March 20 to April 22 to monitor dust events, while in 2008–2009, it was conducted in four separated periods, i.e., March 21, 2008, to April 18, 2008; July 21, 2008, to August 22, 2008; October 15, 2008, to November 15, 2008; and January 15, 2009, to February 15, 2009, to represent the four seasons of spring, summer, autumn, and winter, respectively. Aerosol samples (the sampling generally lasted for 24 h) were collected on Whatman 41 filters (Whatman Inc., Maidstone, UK) by medium-volume samplers (model: (TSP/PM_{10}/$PM_{2.5}$)-2, flow rate: 77.59 L min^{-1}). All the samples were put in polyethylene plastic bags immediately after sampling and then stored in a refrigerator before the weighing and chemical analysis. All the filters were weighed before and after sampling with an analytical balance (Sartorius BT 25 s, reading precision: 10 μg) after stabilizing under constant temperature (20 ± 1 °C) and humidity (40 ± 2 %) for over 48 h. All the procedures were strictly quality controlled to avoid any possible contamination of the samples.

2.2. Chemical analysis

2.2.1. Ion analysis

One-fourth of each sample filter and blank filters were extracted ultrasonically by 10 ml deionized water (18 MΩ cm^{-1}). SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} were analyzed by an Ion Chromatography (Dionex ICS 3000, USA), which consists of a separation column (Dionex Ionpac AS 11 for anion, Dionex IonPac CS 12A for cation), a guard column (Dionex Ionpac AG 11 for anion, Dionex IonPac AG 12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). The detailed procedures were given elsewhere (Yuan et al., 2003).

2.2.2. Element analysis

Half of each sample filter and blank filters was digested at 170 °C for 4 h in a high-pressure Teflon digestion vessel with 3 ml concentrated HNO_3, 1 ml concentrated $HClO_4$, and 1 ml concentrated HF. After cooling, the solutions were dried and then diluted to 10 ml with deionized water (18 MΩ cm^{-1}). Eighteen elements including Al, Fe, Mn, Mg, Ti, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, and As were determined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures were given elsewhere (Zhuang et al., 2001).

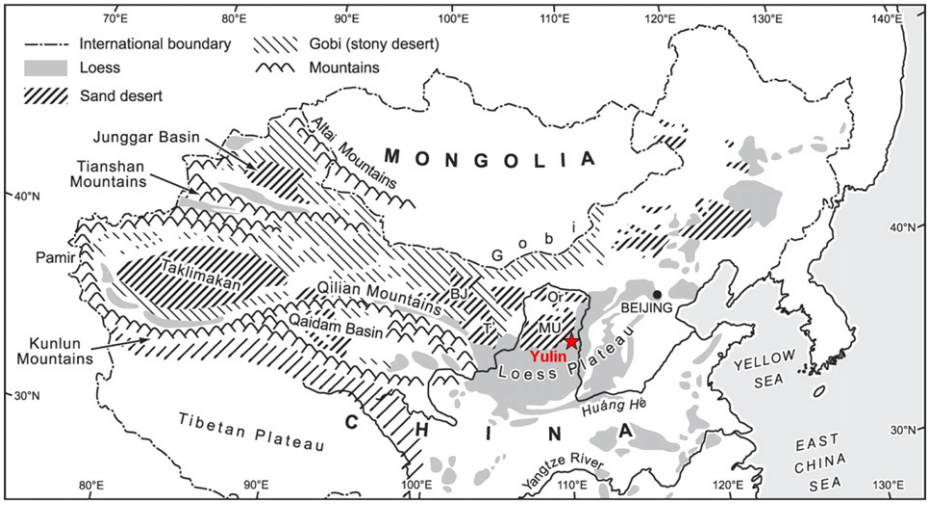

Fig. 1. The location of the sampling site (Yulin, Shaanxi province, China) indicated by the red star. The background map is modified based on the chapter "The Loess Plateau Geography 5" from WordPress.com (https://geog5loessplateau.wordpress.com/).