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A multi-year evolution of aerosol chemistry impacting visibility and haze formation over an Eastern Asia megacity, Shanghai

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HIGHLIGHTS

- Visibility and haze frequency were not improved in Shanghai during 2004–2008.
- Haze caused by secondary inorganic pollution induced the lowest visibility.
- $CaSO_4$ and $Ca(NO_3)_2$ in aerosol were gradually replaced by $(NH_4)_2SO_4$ and NH_4NO_3.
- Evolution of aerosol chemical species caused negligible improvement of visibility.

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ABSTRACT

A multi-year (2004–2008) study of horizontal visibility and factors controlling its variations was conducted in Shanghai. The seasonal average visibility in spring, summer, autumn, and winter was 7.7 km, 8.4 km, 8.1 km, and 6.5 km, respectively, significantly exceeding the haze criteria of 10 km throughout all four seasons. Although SO_2 and NO_2 concentrations gradually shifted to lower levels on an annual basis, no distinct improvement of the annual mean visibility was noticed. Via a grouping method, it was found that the water soluble ions and black carbon were the major contributors to haze formation while the role of mineral aerosol was negligible. Of the ions, SO_4^{2-}, NO_3^-, NH_4^+, K^+, and $C_2O_4^{2-}$ were most associated with the formation of heavy haze. SO_4^{2-} and NO_3^- were both found to have significant decreasing trends with annual decreasing rates of 0.96 and 0.56 μg/m^3/yr, respectively. Conversely, NH_4^+ showed a significant increasing trend with the annual increasing rate of 0.52 μg/m^3/yr. Based on a quantitative correlation analysis, the roles of NH_4^+ and Ca^{2+} on the acids neutralization were almost equivalent in the earlier years of 2004–2005. While the role of Ca^{2+} had tremendously dropped to less than 23% in the later years of 2006–2008. Intense control measures on the emissions of construction works and roadside dust were the main driving force for the evident decreasing trend of annual Ca^{2+} concentrations. This study found that the gradual replacement of $CaSO_4$ and $Ca(NO_3)_2$ by $(NH_4)_2SO_4$ and NH_4NO_3 in aerosol was the major cause of no improvement of the visibility impairment in Shanghai during recent years.

1. Introduction

Haze is an apparent symptom of visibility degradation. The major contributors to haze, e.g. the gaseous precursors and particulate matter, have attracted intensive interests due to its impact on cloud formation, public health, agriculture, and even global climate change (Chen et al., 2003; Kang et al., 2004; Schichtel et al., 2001). The formation of haze is closely related to atmospheric pollution and meteorological factors (Watson, 2002). Generally, haze forms from both excessive primary aerosol emitted

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from anthropogenic sources and the gas-to-particle transformed second aerosol (Chameides et al., 1999; Watson, 2002). The effect of emissions-controls on visibility in southern California was simulated and it was found that the secondary aerosol species were the major cause of significant visibility reduction (Kleeman et al., 2001). Kang et al. (2004) investigated the chemical characteristics of acidic gas pollutants and $PM_{2.5}$ species during hazy episodes in Seoul, South Korea. They found that major ionic species, NO_3^-, SO_4^{2-}, and NH_4^+, and organic materials were the two biggest contributors to $PM_{2.5}$. Chen et al. (2003) studied the summer haze in the mid-Atlantic region. They observed high fractions of SO_4^{2-} (~60%) and signified the role of SO_4^{2-} in haze formation.

Marked decline of visibility and increase of the occurrence frequency of haze have been recorded over many urban areas in developed countries from the 1960s to 1980s (Cass, 1979; Vinzani and Lamb, 1985). Great efforts have been made to reduce the emissions to improve the visibility during the past several decades. It was reported that the visibility improved due to the reduction of pollutant emissions in the United States and Europe since the 1980s (Wang et al., 2009). Schichtel et al. (2001) investigated patterns and trends of haze over the United States from 1980 to 1995 and found that the haze decline was consistent with reductions of $PM_{2.5}$ and sulfur emissions. A massive decline (about 50% in 30 years) of low-visibility occurrences during the past 30 years throughout Europe was also found, and the decline was spatially and temporally correlated with trends in sulfur dioxide emissions (Vautard et al., 2009).

Based on the long-term remote sensing products from SeaWiFS from January 1998 to December 2010, the annual trends of AOD (Aerosol Optical Depth, 550 nm) at both global and regional scales were compared (Hsu et al., 2012). Except for the Arabian Peninsula, which was mainly impacted by dust, the three regions of China (i.e. northern, southern, and eastern) showed the largest positive trends affected by the human activities throughout the world. Visibility degradation has spread over not only the industrial and populous areas in China (e.g. the North China Plain, the Yangtze River Delta, and the Pearl River Delta) but also central and western China caused by the rapid urbanization and motorization (Kaiser and Qian, 2002). Shortwave radiation at various ground stations in China during the period of 1971–2000 have been going through obvious decreasing trends with the greatest decreases occurring in the central and eastern coastal regions of China (Streets et al., 2008). Che et al. (2007) stated that the horizontal visibility had been significantly decreased in China during 1981–2005, and the increased aerosol loadings were responsible for visibility degradation. Significant anti-correlations between $PM_{2.5}$ concentration and visibility had been revealed in various cities of China, e.g. Beijing (Wang et al., 2006a), Jinan (Yang et al., 2007), Guangzhou (Tao et al., 2009) and Shanghai (Huang et al., 2012b). However, most of the research focused on the relationship between visibility trends and bulk aerosols, rare studies revealed the internal reason of a certain phenomena and gave persuasive explanations.

We choose Shanghai as a typical area to be further explored in this study, as it is the most populous and economically vigorous region in China. Shanghai is located on the eastern tip of the Yangtze River Delta (YRD), which is one of the most industrialized cities with the largest adjacent metropolitan areas in the world. The GDP (Gross Domestic Product) of Shanghai increased five fold in the decade from 1996 to 2006 and the numbers of automobiles increased from 0.47 to 2.53 million during these years (UNEP, 2009). Shanghai has long suffered from visibility impairment as a result of intense industrial and domestic pollutant emissions with high humidity (Huang et al., 2012a, 2012b). During the past decade, especially during the China's 11th Five-Year-Plan, China emphasized on the reduction of SO_2 emission. Also, when the local government prepared for the 2010 Shanghai World Expo, great efforts have been made to reduce emissions in Shanghai (Lin et al., 2013). In this study, the inter-annual variation of visibility and occurrence frequency of haze from 2004 to 2008 in Shanghai is presented. The evolution of the frequency distribution patterns of major pollutants (i.e. SO_2, NO_2 and PM_{10}) is examined to explain the inter-annual trend of visibility. The progression of aerosol chemical species is further investigated to reveal the causes of the visibility decrease and the relationship between visibility degradation and aerosol components. The observational evidences are suggested to design effective control strategies for visibility improvement.

2. Methodology

2.1. Observational site

The observational site (31.3°N, 121.5°E) in this study is on the roof (~20 m) of a teaching building on the campus of Fudan University in Yangpu District of Shanghai. Almost no high buildings were around this sampling site. More than 20 million residents (13 million residents with registered permanent residence plus more than 10 million without permanent residence) are living in this area. This site could be regarded as representative of the megacity, standing for the mixing of emissions from residential, traffic, construction, and industrial sources (Huang et al., 2013).

2.2. Aerosol sampling and chemical analysis

Aerosol samples of TSP and $PM_{2.5}$ were collected on Whatman® 41 cellulose acetate filters (Whatman Inc., Maidstone, UK) using medium-volume samplers manufactured by Beijing Geological Instrument-Dickel Co., Ltd. (model: TSP/PM_{10}/$PM_{2.5}$–2; flow rate: 77.59 l min^{-1}). An inter-comparison study of different types of filters showed that the cellulose acetate filters could quantitatively collect and retain the semi-volatile compounds such as ammonium nitrate aerosol (Schaap et al., 2004). One-month samples were collected in each season from 2004 to 2008: spring (March 15–April 15), summer (July 15–August 15), autumn (October 15–November 15), and winter (December 15–January 15). The duration time of the daily sampling was generally 24 h. More samples with shorter duration time were collected during heavy polluted days. Filters were taken back to the laboratory as soon as each day's sampling was over, and preserved in the refrigerator under a temperature of less than 4 °C to prevent the loss of any aerosol compounds as far as possible. The filters before and after sampling were weighed using an analytical balance (Model: Sartorius 2004MP) with a reading precision of 10 μg after stabilizing under constant temperature (20 ± 1 °C) and humidity (40 ± 1%) in a chamber for 48 h. All the procedures were strictly quality controlled to avoid the possible contamination of samples.

Eleven inorganic ions (SO_4^{2-}, NO_3^-, F^-, Cl^-, NO_2^-, PO_4^{3-}, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and four organic acids (formic, acetic, oxalic, and methylsulfonic acid (MSA)) were analyzed by Ion Chromatography (ICS 3000, Dionex), which consisted of a separation column (Dionex Ionpac AS 11), a guard column (Dionex Ionpac AG 11), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50) and a gradient pump (Dionex Ionpac GP50). The detail procedures were given elsewhere (Yuan et al., 2003).

A total of 20 elements (Al, Fe, Mn, Mg, K, Ti, Sc, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, and As) were analyzed. Half of each sample and blank filter was digested at 170 °C for 4 h in high-pressure Teflon digestion vessel with 3 ml concentrated HNO_3, 1 ml